THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

High temperature mixed-adhesive joints for aerospace applications

by

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Abstract

The use of structural adhesives is extensive in highly advanced structures such as those employed by the aerospace industry. Modern high performance adhesives exhibit several key advantages that make them a very interesting solution for structures where low weight is a main requirement, namely their ability to bond dissimilar materials, their smooth stress distribution and their high fatigue resistance. However, these materials, mostly polymeric in nature, soon reach their limitations when introduced in highly demanding environments, with strong thermal and dynamic loadings.

Heat shields are an aerospace component where adhesives are subjected to these extreme conditions, as they are intended to insulate the internal structure of a vehicle from the heat generated during re-entry into the atmosphere. In this component a ceramic tile must be joined to a metallic structure, and adhesive bonding is the most effective method to join these highly dissimilar materials. The adhesive used for this application is a room temperature vulcanizing (RTV) silicone, which exhibits high temperature tolerance but has extremely low mechanical strength.

To improve this component, an alternative bonding method was explored, where instead of using a single adhesive, two adhesives were combined in the same joint. This concept is known as the mixed adhesive joint. Two adhesives with remarkably different properties can work synergistically and lead to stronger joints with wider temperature envelopes. The mixed adhesive joint studied in this thesis included the same RTV silicone discussed above and combined it with a high performance, high temperature epoxy.

The determination of the mechanical properties of adhesives and substrates was also an important research topic of this work. While many of the adhesives properties were already available from previous publications, the mechanical behaviour of the RTV silicone adhesive was further explored and more of its properties characterized at low temperatures. The properties of the ceramic material were also identified using a specially designed specimen and an inverse method, with the help of a numerical simulation.

During the course of this work a technique to produce ceramic-metal mixed adhesive joints was also developed. A testing procedure was defined and tools were produced to test this novel specimen. The joints were quasi-statically tested at room temperature

and high and low temperatures. Impact testing was also performed to assess the joint behaviour under high strain rates.

Using the previously determined mechanical properties, numerical models representative of the tested joints were developed. These models, made in two and three dimensions, made use of cohesive elements to accurately simulate failure progression in the joint. The models were successfully validated against experimental data and then used to study some alternative configurations and their inherent advantages and disadvantages.

The research developed during the course of this work demonstrates that using modern test procedures and simulation tools it is possible to design strong and durable dual-adhesive ceramic metal joints using high performance adhesives that ensure high performance under a wide range of demands.

Resumo

O uso de adesivos é hoje em dia uma prática corrente na construção de estruturas de alta performance, tais como aquelas usadas na indústria aeroespacial. Isto deve-se ao facto de os adesivos modernos apresentarem importantes vantagens que os posicionam como um método de ligação ótimo para estruturas onde o peso é um fator crítico. Entre essas vantagens contam-se a sua capacidade de unir materiais dissimilares, as distribuições de tensão uniformes e a sua elevada resistência à fadiga. No entanto, a natureza polimérica destes materiais faz com que estes sejam muito limitados quando sujeitos a ambientes adversos, com elevados carregamentos térmicos ou dinâmicos.

Entre os vários componentes aeroespaciais nos quais os adesivos são sujeitos a estas condições exigentes contam-se os painéis de proteção térmica, os quais possuem a função de isolar o veículo do calor que é gerado durante a reentrada na atmosfera. Nesta peça um painel cerâmico deverá ser ligado a uma estrutura metálica e o uso de adesivos perfila-se como o método mais eficaz para unir esses materiais altamente dissimilares. O adesivo aplicado normalmente nesta aplicação é um silicone com vulcanização à temperatura ambiente (usualmente referido como silicone RTV), sendo este um material que exibe elevada tolerância a temperaturas extremas mas apresenta baixa resistência mecânica.

Para melhorar este componente, um método de ligação alternativo foi explorado neste trabalho, recorrendo a dois adesivos combinados na mesma junta ao invés do uso de um único adesivo. Este conceito é conhecido como a junta adesiva mista. Dois adesivos com propriedades significativamente diferentes combinam-se de uma forma sinergética para dar origem a uma junta mais resistente e com uma mais ampla gama de temperaturas de funcionamento. Os adesivos aplicados na junta mista proposta são um adesivo do tipo silicone RTV (já descrito acima) e um epóxi de alta resistência e alta temperatura.

A determinação das propriedades mecânicas dos adesivos e dos substratos foi também um importante tema de pesquisa deste trabalho. Enquanto muitas das propriedades mecânicas já foram determinadas em trabalhos previamente publicados, foram definidas propriedades adicionais do comportamento mecânico do silicone RTV. As propriedades mecânicas do material cerâmico foram também estudadas segundo um método inverso, que requereu um provete cerâmico especialmente desenhado e um modelo de simulação numérica.

Foi também desenvolvida uma técnica para produzir juntas mistas cerâmico-adesivo. Foi definido um procedimento de teste e foram desenhadas ferramentas adequadas para ensaiar o provete. As juntas foram testadas de forma quási-estática à temperatura ambiente a baixas e altas temperaturas. Foram também realizados testes de impacto para estudar o comportamento da junta sob velocidades de deformação elevadas.

Foram produzidos modelos numéricos usando as propriedades mecânicas previamente determinadas. Estes modelos, elaborados em duas e três dimensões, recorreram a elementos coesivos para representar de forma fiel a progressão de dano ao longo da junta. Os modelos foram inicialmente validados com dados experimentais e posteriormente usados para estudar algumas configurações alternativas e as suas inerentes vantagens e desvantagens.

Os dados obtidos durante o curso deste trabalho demonstram que recorrendo a procedimentos de teste modernos, associados a ferramentas de simulação avançadas e ao uso de adesivos de alta performance, é possível projetar juntas mistas resistentes e duráveis, que asseguram excelente comportamento mecânico numa alargada gama de solicitações.

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Contents

List of publications

[1] Marques, E.A.S., da Silva, L.F.M., Banea, M.D., Carbas, R.J.C., **Adhesive joints for low- and high-temperature use: An overview**, *Journal of Adhesion*, Vol. 91(7): pp. 556-585. (2015)

[2] Marques, E.A.S., Banea, M.D, da Silva, L.F.M.,Carbas, R.J.C, C. Sato, **Effect of Low Temperature on Tensile Strength and Mode I Fracture Energy of a Room Temperature Vulcanizing Silicone Adhesive**, *Journal of Testing and Evaluation*, Vol. 44 (3). (2016)

[3] Marques, E.A.S., Magalhães, D.N.M., da Silva, L.F.M., **Experimental study of silicone-epoxy dual adhesive joints for high temperature aerospace applications** *Materialwissenschaft und Werkstofftechnik*, Vol. 42(5): pp. 471-477. (2011)

[4] Marques, E.A.S., da Silva, L.F.M., Sato, C.: **Testing of dual adhesive ceramic-metal joints for aerospace applications**. In: Kumar, S., Mittal, K.L. (eds.) Advances in modelling and design of adhesively bonded systems, pp. 170–190. Beverley MA. (2013).

[5] Marques, E.A.S., da Silva, L.F.M., Flaviani, M., **Testing and simulation of mixed adhesive joints for aerospace applications,** *Composites Part B: Engineering*, Vol. 74: pp. 123-130. (2015)

[6] Marques, E.A.S., Campilho, R.D.S.G, da Silva, L.F.M., **Geometrical study of mixed adhesive joints for high temperature applications,** *Journal of adhesion science and technology*, DOI: 10.1080/01694243.2015.1121801

1 Introduction

1.1. Background and motivation

Adhesive joints are a joining method whose importance and usage have increased significantly during the last decades. While initially seen as more suitable for low strength applications, the development of stronger and more durable adhesives has made their use a valid option for several structural applications [1].

Adhesive joints exhibit several important characteristics that make them uniquely suited for some applications. The aerospace industry has always been one of the main proponents of the use of adhesive joints, mainly due to its constant focus in creating structures with extremely high strength-to-weight ratios. Adhesives, which are almost all polymeric in nature, have low densities, which combined with thin joint thicknesses, allow the design of joints which are very light. With the appearance of high strength modern adhesives, it became possible to design connections that weigh very little but are still able to offer strength equiparable with any other conventional joining method.

Another fundamental reason behind the use of adhesive joints by the aerospace industry is this technique’s inherent capability to effectively join dissimilar materials. With a careful selection of adhesives associated with any required surface preparation, there are almost no limits to the materials that can be bonded together. This positions adhesive joints as a prime technique for use in multi-material structures. This type of structure is currently very prevalent in the aerospace sector, where the combination of composites, plastics and metallic alloys is often the only option for delivering a design capable to achieve every design goal.

One critical aerospace subsystem that uses multi-material design is the thermal protection system, used for the protection of vehicles from the high temperatures sustained mainly during the re-entry into the atmosphere phase [2]. Various types of designs exist for solving this problem, almost all of them consisting of the installation of some type of heat resistant material on the external skin of the vehicle. This material insulates or absorbs the energy resulting from the re-entry friction, keeping the underlying structure of the vehicle cool. Due to their nature, the insulating materials are quite different from the materials that comprise the aerospace vehicle structure and therefore the construction of the heat shield demands a joining technique that is able to join two very dissimilar materials.

A well-known technique for heat shielding in aerospace application is the use of a ceramic heat shield bonded to an aluminium skin. Figure 1 shows a schematic representation of the bonding method. This method was employed for decades on the United States Space Shuttle but several failures occurred. In 2003, several ceramic tiles detached from the Columbia shuttle on ascent. One week later, during re-entry, the resultant overheating led to the complete loss of the vehicle and its crew. The failure was blamed on the impact of an insulating foam against the ceramic tiles, which completely removed a section of tiles from the underbelly of the vehicle [3].

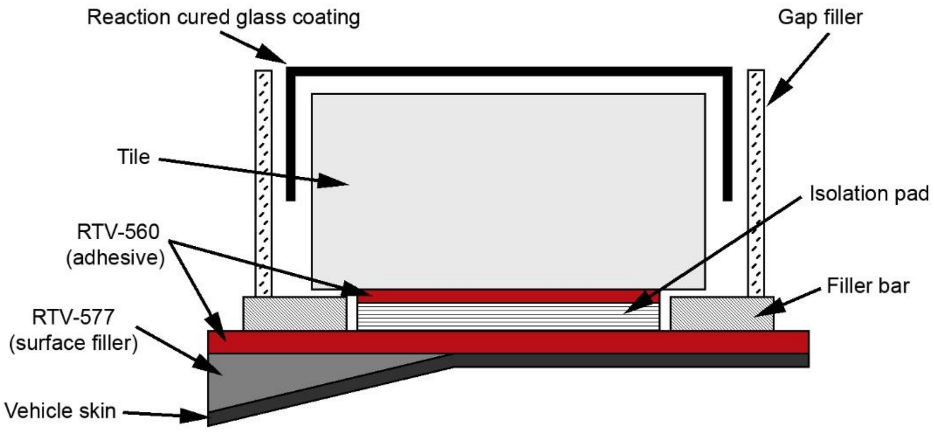

Figure 1 - Schematic drawing of the heat tile bonded assembly on the Space Shuttle

This failure illustrates the importance of bonding in the aerospace sector. Many critical applications depend on adhesive joints and it is important to ensure that the joints are durable and strong enough to resist damage. Due to the extreme environmental demands, constant research in materials and joint geometry is fundamental to increase the safety of aerospace systems.

In the Space Shuttle design, the ceramic tiles are bonded using a RTV silicone adhesive [4]. This material is closer to a sealant than a structural adhesive. Its mechanical strength is very low and it even decreases as the temperature increases. However, while the strength is low, few adhesives can provide comparable strength at high temperatures and still maintain an important amount of flexibility and the capability to accommodate the thermal expansion of the whole structure.

This compromise leads to a relatively weak joint that might be improved using more advanced adhesive joint designs. One of the most promising and well suited techniques for this application is the use of a dual adhesive joint. Raphael [5] first proposed this technique as a solution to reduce stress concentration at the ends of the joint overlap. By introducing a more flexible adhesive at the ends of the overlap and using a stiffer stronger adhesive in the central section, improvements in joint strength can be attained. The flexible adhesive withstands the more extreme deformations on the joint ends while the stiff adhesive is able to work better under the reduced deformations of the joint's central section.

Subsequent research has also turned the mixed adhesive joint into a very capable solution, able to work under high thermal loadings. If adhesives are selected with regard to their optimal working temperature ranges, it is possible to greatly widen the temperature range of the complete adhesive joint, greatly improving thermal protection. This was first predicted in 1973, when Hart-Smith [6] recognized that the use of mixed adhesive joints could yield significant improvements in mechanical strength for joints subjected to large temperature gradients. In 2007, da Silva and Adams [7, 8] further expanded this concept and predicted improvements in the mechanical behaviour of a joint under a large temperature gradient. Figure 2 shows the working principle of this type of joint. For the first time, the adhesives to be combined were not only dissimilar in the mechanical properties, but also differed in their temperature handling capabilities.

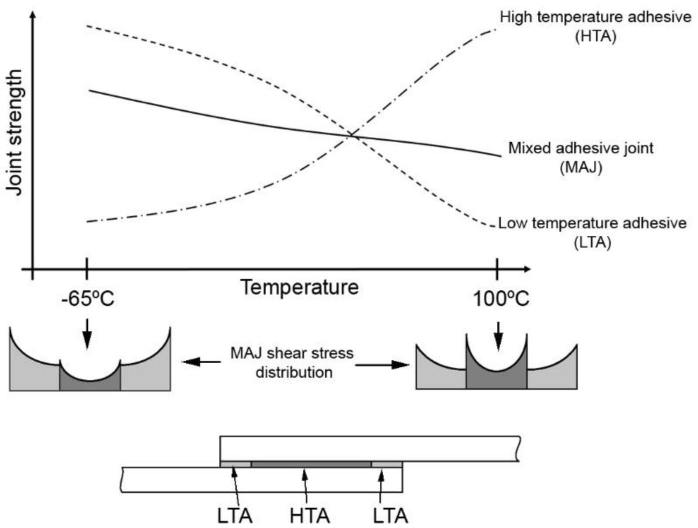

Figure 2 -Dual adhesive joint concept

1.2. Problem definition

As previously described, thermal protection systems are an aerospace application where the use of adhesives is almost a requirement due to the dissimilar materials used. These systems need a strong and durable connection between ceramic tiles and the metallic structure of the vehicles external skin. In the Space Shuttle the bonding was accomplished by means of a RTV silicone, but the low strength of this material might lead to failure and detachment of the tiles in unpredicted situations. Stronger and stiffer adhesives might seem like a valid solution, but these materials become extremely brittle in the low temperatures encountered during the orbital phases.

The solution proposed in this thesis is the use of a dual adhesive joint, combining a strong and stiff epoxy adhesive with a more flexible silicone adhesive. The silicone adhesive allows the joint to maintain its flexibility at low temperatures and does not suffer damage at high temperatures, while the epoxy is suited to the high temperature portions of the operational envelope. If this synergetic effect can be harnessed, this is result in a stronger joint, able to function safely in a wider range of temperatures and under more demanding mechanical loadings.

The main goal of this work is therefore the design of an improved metal-ceramic joint, using dual adhesives and able to function safely as a thermal heat shield, bringing improvements over the conventional solution. However, the design of a dual adhesive joint is complex and demands careful work on various engineering aspects.

The first of these fundamental aspects is the knowledge of the material properties. While the selection of the adhesives can be performed with commonly available information regarding the adhesives mechanical behaviour, to accurately model the dual adhesive joint more detailed tests are needed. Much of the characterization work regarding the adhesives studied in this thesis has been performed already in a previous PhD thesis by Mariana Banea and subsequent publications, but the need to characterize some fundamental material properties still remains.

The selection of the joint geometry is another important issue. The possible correlation between laboratory results and a real world application depends strongly on the quality of the design of the test specimen. The manufacture procedure of this specimen is also a challenge, as it requires the development of an accurate way to position the substrates, a method to separate and regulate the adhesive layers and a controlled curing method. The testing phase is yet another challenging part of the work. The testing devices employed must subject this non-standardized joint to a mechanical loading at various temperatures in a reliable and controlled fashion.

The last main step is the use of the finite element method to accurately simulate the behaviour of a ceramic-metal joint. Using the mechanical properties previously obtained, a model can be developed that allows a numerical study to be undertaken, with the aim of adjusting the joint properties and behaviour.

1.3. Objectives

The main objective of this research is the development of an adhesive joint to bond a ceramic tile to an aluminium substrate and respective testing at low temperature, high temperature and under impact loadings. Therefore, this main objective can be divided in several specific sub-objectives.

- Measure the unknown mechanical properties of the adhesives used (RTV silicone and epoxy adhesive.
- Design a ceramic-metal joint geometry to simulate and approximate a real world application of this technology.
- Develop a testing procedure and design all the necessary tools to enable the testing of the ceramic-metal joint at various temperatures and under all relevant types of mechanical loadings.
- Use the testing procedure to compare the mixed adhesive joint with single adhesive joints and use these tests to understand the behaviour, advantages and disadvantages of the mixed adhesive joints.
- Use finite element techniques to study the joint behaviour and optimize the joint strength and behaviour.

1.4. Research methodology

To achieve the objectives listed above, the following methodology was used:

- A literature review was undertaken, focusing on the previous research on the field of adhesive joints for large temperature gradients. The relevant adhesive and substrate properties, manufacturing and testing techniques were studied. Numerical and analytical methods for the strength prediction of this type of joint were also focus of attention. This is presented in **Paper 1.**
- The adhesive and substrate mechanical properties that were not available in literature or previous research were determined using failure strength tests and fracture tests. These tests were performed at various temperatures to allow the understanding of the materials behaviour along the temperature range under consideration. Adhesive property determination can be found in **Paper 2**, while some substrate properties can also be found in **Paper 5.**
- Experimental joint geometries were selected and the manufacturing techniques were developed and refined. Failure strength tests of complete joints at various temperatures were followed by impact tests. These procedures are shown and described in **Paper 3** and **Paper 4**.

- A two dimensional (2D) finite element model of the joints was developed and used to validate the mechanical properties. This model made use of cohesive element modelling and was compared with experimental testing results of the complete joint. This is shown in **Paper 5**.
- To be able to propose an optimized geometry for the metal-ceramic dual adhesive joint, a more powerful three dimensional (3D) finite element model was developed, again making use of cohesive elements to simulate the failure on the adhesive layer. Varied alternative joints configuration were simulated and their merits discussed. **Paper 6** explains the work flow of this step.

1.5. Outline of this thesis

This thesis consists of six appended papers and a summary.

Paper 1 Marques, E.A.S., Da Silva, L.F.M., Banea, M.D., Carbas, R.J.C., **Adhesive joints for low- and high-temperature use: An overview**, Journal of Adhesion, 91 (7): pp. 556-585 (2015).

Abstract of Paper 1: This work presents a review of several investigations on the topic of adhesive bonding at high and low temperatures. Durability and strength at extreme temperatures have always been a major limitation of adhesives that, given their polymeric nature, exhibit substantial degradation at temperatures where other structural materials (such as metals for example) have minute changes in mechanical properties. However, due to the inherent advantages of bonding, there is a large and continued effort aiming to improve the temperature resistance of adhesive joints, and this effort has been spread among the various topics that are discussed in this review. These topics include adhesive shrinkage and thermal expansion, adhesive properties, joint geometry optimization, and design techniques, among others. The findings of these research efforts have all found use in practical applications, helping to solve complex problems in a variety of high-tech industries where there is a constant need to produce light and strong components that can withstand large temperature gradients. Therefore, the final sections of this work include a discussion on two specific application areas that demonstrate the strict demands that extreme temperature use imposes on adhesive joints and the methods used to improve their performance.

Paper 2 Marques, E.A.S., Banea, M.D, Da Silva, L.F.M.,Carbas, R.J.C, Sato, C. **Effect of Low Temperature on Tensile Strength and Mode I Fracture Energy of a Room Temperature Vulcanizing Silicone Adhesive**, Journal of Testing and Evaluation, 44 (3) (2016).

Abstract of Paper 2: Aerospace applications have an increasing demand for strong and reliable adhesives, able to withstand large temperature gradients. The variation of the adhesive's mechanical properties with temperature is therefore one of the factors that must be well understood before safe and reliable adhesive joints can be designed for these applications. The stress-strain curve and the toughness properties of an adhesive show strong dependency with temperature for most adhesives, especially near the glass transition temperature (T_g). In this work, an experimental procedure is undertaken to evaluate the effect of low temperatures on the adhesive strength and mode I fracture toughness of a room temperature vulcanizing silicone (RTV) adhesive. Firstly, the temperature at which the T_g of the RTV occurs was obtained by means of an in-house developed measurement apparatus. Bulk specimens were manufactured and tested at temperatures above and below the T_g in order to obtain a strength envelope of the adhesive over this large temperature range. Single lap joints were also manufactured with this adhesive to assess the behaviour of the adhesive when assembled in a complete joint. For the determination of pure mode I fracture toughness, Double Cantilever Beam specimens were also tested at negative temperatures near T_g. The results showed that the failure loads of all the tests performed have strong temperature dependence and this must be taken into account during adhesive joint design using this type of adhesives.

Paper 3 Marques, E.A.S., Magalhães, D.N.M., Da Silva, L.F.M. **Experimental study of silicone-epoxy dual adhesive joints for high temperature aerospace applications** Materialwissenschaft und Werkstofftechnik, 42 (5): pp. 471-477 (2011).

Abstract of Paper 3: Adhesive bonding is extensively used in aerospace applications. Some of the most important aerospace applications are in heat shields intended to protect metallic structures from extreme heat. Many heat shields are bonded with RTV

silicone based adhesives, which have excellent resistance to high temperature but very low strength. This work proposes and studies three alternate configurations to these adhesive layers. One with only RTV silicone (RTV106), one with only a high temperature epoxy (XN1244) and finally another configuration introducing both adhesives in the same joint (mixed joint). Experimental specimens and a testing device intended to simulate the loads on an actual heat shield were manufactured. These specimens were subjected to loading and tested until failure at both low and high temperatures. It was demonstrated that while the RTV silicone joints lose strength at 100ºC, the epoxy and mixed joints are able to retain most of their strength. The mixed joint is also able to withstand large values of displacement at relatively high forces, indicating excellent capabilities at absorbing directed energy. The improvements and advantages deriving from the use of these alternative configurations are described and compared.

Paper 4 Marques, E.A.S., da Silva, L.F.M., Sato, C.: **Testing of dual adhesive ceramic-metal joints for aerospace applications**. In: Kumar, S., Mittal, K.L. (eds.) Advances in modelling and design of adhesively bonded systems, pp. 170–190. Beverley MA (2013).

Abstract of Paper 4: Aerospace structures are often complex combinations of high performance materials, carefully optimized to withstand extreme working conditions. Aerodynamic forces, wide temperature range, vacuum and impacts are powerful forces that require these structures to be designed using only the strongest materials and most reliable construction techniques. Among these structures are heat shields for aerospace applications, components comprised of various layers, intended to protect the metallic structures of a vehicle from high temperatures. This work proposes and studies three alternate configurations to these layers, using adhesives to bond the shield together: one configuration with RTV silicone only (RTV106), one with only a high temperature epoxy (XN1244) and finally another configuration introducing both adhesives in the same joint (mixed joint). Experimental specimens and a testing device intended to simulate the loads on an actual heat shield were fabricated. These specimens were subjected to loading and tested until failure at three different temperature levels (-65ºC, 25ºC, 100ºC). Impact testing was also performed to assess the suitability of each configuration to withstand direct impacts.

Paper 5 Marques, E.A.S., da Silva, L.F.M., Flaviani, M., **Testing and simulation of mixed adhesive joints for aerospace applications**, Composites Part B: Engineering, 74: pp. 123-130 (2015).

Abstract of Paper 5: An important aerospace application of adhesives is in heat shields intended to protect metallic structures from heat. Heat shields ceramic tiles are bonded with a room temperature vulcanizing silicone adhesive, which has high temperature resistance but low strength. Previous works proposed mixed adhesive joints as a viable solution, therefore an investigation of this technique was performed.

This work studies three adhesive joint configurations: joint with RTV silicone only, joint only with high temperature epoxy and a joint introducing both adhesives in the same joint (mixed joint). The aim of the research was to simulate the load on a heat shield and predict the joint strength. Finite element models were developed using a triangular cohesive law including initiation, softening and failure. Numerical results were compared with experimental results. Properties of the ceramic were obtained with an inverse method. There was a good agreement between experimental and numerical data, showing that this technique could be used for load prediction and optimization of this type of models.

Paper 6 Marques, E.A.S., Campilho, R.D.S.G, da Silva, L.F.M., **Geometrical study of mixed adhesive joints for high temperature applications**, *Journal of adhesion science and technology*, DOI: 10.1080/01694243.2015.1121801

Abstract of Paper 6: The use of adhesives for high performance, structural applications has significantly increased in the last decades, allowing the aerospace and automotive industries to construct lighter and more efficient multi-material structures. However, the use of adhesive joints in adverse environmental conditions is still limited, due to the reduced capability of adhesives to withstand large thermal gradients. Dual adhesive joints, which contain two adhesives with remarkably different mechanical behaviour, are suitable for being used in extreme temperatures. The object of this study is a ceramic-metal joint, representative of the thermal protection systems of some aerospace vehicles. In this paper, several joint mixed joint geometries are presented, studied with recourse to finite element analysis. In a first phase, the 3D finite element models and the material properties are validated against experimental data. In a second phase, the model geometry is modified, with the aim of understanding the effect of several changes in the joints mechanical behaviour and comparing the merits of each geometry. The models presented good agreement was found between experimental and numerical data and the alternative geometries allowed the introduction of additional flexibility on the joint but at the cost of lower failure load.

2 Adhesives tested

This thesis is based upon the concept of the dual-adhesive joint, where a pair of adhesives work synergistically and where the end result is a joint exhibiting properties unattainable by any one of the two adhesives working alone. Therefore, the selection of the adhesives was critical for the success of this work.

As mentioned before, this thesis was preceded by another thesis fundamentally concerned with the properties of the adhesives used in this thesis. However, the adhesive selection was done in strict cooperation between the authors of both theses. This chapter explains the reasoning behind the adhesive selection procedure and provides information on the properties already determined for each adhesive while listing those that remained to be tested.

The dual adhesive joint concept requires the selection of a low-temperature adhesive and a high temperature adhesive, with dissimilar mechanical properties. The low temperature adhesive must be flexible and ductile at low temperatures, while not suffering degradation at high temperatures. In contrast, the high temperature adhesive must exhibit optimal performance at high temperatures, with some degree of ductility and high mechanical strength.

For this work, the high temperature adhesive is an epoxy, while the selected low temperature adhesive is a room temperature vulcanizing (RTV) silicone. Both adhesives are described in detail in the following sections.

2.1 High temperature adhesive – High temperature epoxy

The selected epoxy is a commercially available stiff and brittle adhesive, suitable for high temperature use produced by Nagase-Chemtex (Osaka, Japan) under the reference XN1244. This adhesive is a one component, high temperature, paste epoxy adhesive, with a high glass transition temperature (T_g). Due to its high T_g it provides good mechanical properties up to 150ºC. The cure process is heat activated, requiring temperatures around 140ºC during one hour to achieve complete cure [9].

The room temperature mechanical properties of this adhesive were published by Banea et al. [9-11] and are listed in Table 1.

Table 1 – XN1244 adhesive properties at room temperature [9-11]

Property	XN1244 epoxy
E - Young's Modulus (N/mm^2)	5870
G - Shear Modulus (N/mm^2)	2150
t_n^0 - Tensile Strength (N/mm^2)	68.23
t_s^0 - Shear Strength (N/mm^2)	37
G_n^c - Mode I fracture energy (N/mm)	0.47
G_s^c - Mode II fracture energy (N/mm)	2.2

2.2 Low temperature adhesive – Room temperature vulcanizing silicone

The RTV silicone used in this work is of a commercially available type, produced by ACC Silicones LDT (Bridgewater, UK) under the reference RTV106. This adhesive is very distinct from the XN1244 epoxy by being a very ductile and flexible material, with much lower mechanical strength. It is however much more insensitive to extremely low temperatures, maintaining a good level of strength while the epoxy becomes extremely brittle [12].

The curing process of the RTV106 adhesive is very distinct from the curing process of the XN1244 epoxy, being based on the absorption of humidity from the air. To ensure a complete cure, water molecules must diffuse from the surface of the material to the interior. Due to the reduced mobility of these water molecules, this cure is necessarily a slower process. When thick layers of adhesive are used, as many as 10 days can be required to obtain full cure.

As for the epoxy adhesive, the room temperature mechanical properties of these adhesives were published by Banea et al. [12-14] and are listed in Table 2.

Table 2 – RTV106 adhesive properties at room temperature [12-14]

Property	RTV106 silicone
E - Young's Modulus (N/mm^2)	1.6
G - Shear Modulus (N/mm^2)	0.86
t_n^0 - Tensile Strength (N/mm^2)	2.3
t_s^0 - Shear Strength (N/mm^2)	1.97
G_n^c - Mode I fracture energy (N/mm)	2.73
G_s^c - Mode II fracture energy (N/mm)	5

3 Test methods

Experimental testing is a task of great importance during research in the field of adhesive joints. Due to the large variety in adhesive types and their properties as well as the large amount of different possible substrates, surface preparations and curing procedures, there is the need to validate experimentally any new bonding procedure. Doing so will ensure that each part of the joint is working correctly and its potential is fully exploited, avoiding costly failures further on. Experimental testing was extensively performed during the course of this work.

These experimental tests can be divided into main groups, some tests measuring the properties of the adhesives in bulk while others evaluate the strength of complete joints. A variety of bulk tests were employed to determine material basic properties. These focused on the properties of adhesives (**Paper 2**) and the ceramic (**Paper 5**). The remaining tests focused on the evaluation of the strength and deformation of complete joints, comprised of substrates and adhesive, allowing comparison studies between joints with different designs and materials. Such tests are included in **Paper 3**, **Paper 4** and **Paper 5**.

The main tests used are described in the following sections.

3.1 Bulk specimen tensile testing

Bulk tests use a specimen with a specific shape (informally called a “dogbone” specimen), obtained from a cured sheet of adhesive. These specimens are tested under tensile loads, with the load and displacement being registered and used to create a stress-strain curve. This curve can then be used to extract elastic moduli, tensile strength and assess ductility.

A variety of standards exist, specifying the shape of the specimen and the testing conditions. Standard BS 2782 [15] was used to test RTV106 silicone adhesive. This standard has a shape suitable to flexible materials, which is the case of the silicone adhesive tested in this work, shown in Figure 3.

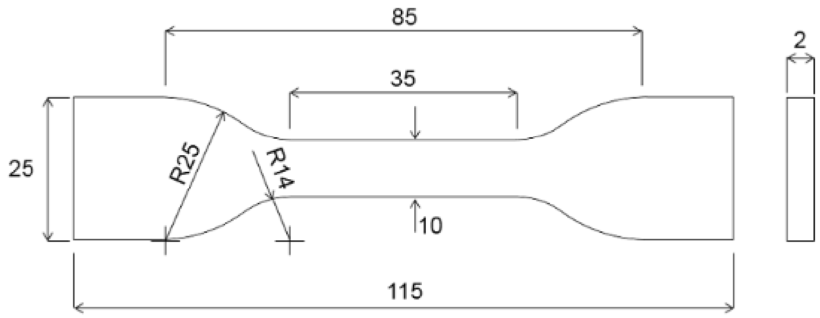

Figure 3- Bulk specimen geometry (dimensions in mm)

The manufacture of such specimens is a complex process, mainly due to the difficulty in obtaining a specimen that is not only geometrically accurate but also devoid of defects. Any void, crack or section with incomplete cure leads to erroneous and unreliable results.

Bulk specimens of stiff adhesives are manufactured from a sheet of adhesive material, cured under isostatic pressure, which is then machined to its final shape using a milling machine [16]. However, RTV silicone specimens are soft and flexible, and cannot be accurately machined. Therefore, the manufacture process of these specimens uses an in-house designed mould that allows the adhesive to be directly moulded into its final shape [17]. This mould consists of a central plate, with the shapes of the specimen's cut into it, as shown in Figure 4. This central plate is mounted between two thicker steel plates, which are the base plate and the top plate. The free volume in the central plate is limited by the two other plates, therefore defining the final shape of the specimen. It was found that introducing a thin silicone rubber sheet between the central plate and the base plates helped to obtain higher quality specimens due to the compressive force of the silicone rubber. The rubber sheet also helps to avoid any adhesion between the mould and the specimen.

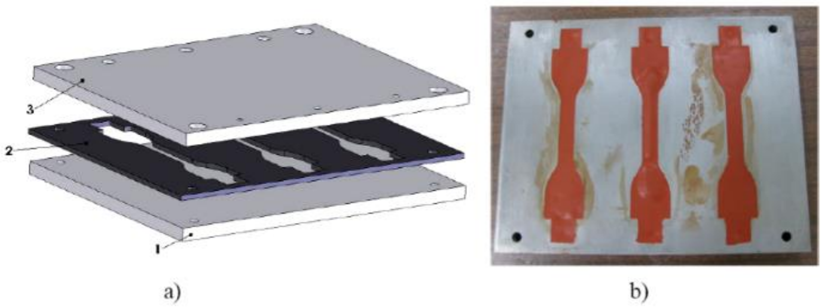

Figure 4- a) Mould for bulk specimen manufacture. b) Bulk specimens in mould

To produce the specimen, the adhesive is then applied in the cavities of the central plate, the upper plate is closed and the mould is placed into a hydraulic press. This compresses the silicone and helps removing air bubbles and excess adhesive. The specimens are left to cure inside the mould and then removed when cured.

3.2 Double cantilever beam (DCB) specimen testing

During the course of this work, the strength of adhesive joints is predicted using cohesive damage models. To be able to use these models, it is important to measure the fracture properties of the materials, namely the fracture toughness. The fracture toughness is dependent on the type of loading (mode I, mode II, mode III or mixed mode). While there are many alternative methods, the fracture toughness is usually measured under mode I using the double cantilever beam (DCB) test and under mode II using the end notched failure (ENF) test. Procedures have also been devised to measure the fracture toughness directly under mixed mode conditions [18]. For this thesis, only mode I fracture tests were performed, to obtain relevant properties of RTV106 specimens. A description of the DCB test follows.

The DCB test is a standardized test, first introduced in ASTM D3433 standard [19] and later adopted by ISO in ISO 2009 standard [20]. The DCB specimen is of quite simple construction, consisting of two parallel beams bonded lengthwise by an adhesive layer (Figure 5). A vertical load is applied at the ends of the beams, forcing their separation and creating a crack that gradually progresses through the adhesive layer. If stable crack propagation exists, the load-displacement curve obtained can be processed to obtain the fracture energy of the adhesive layer in mode I.

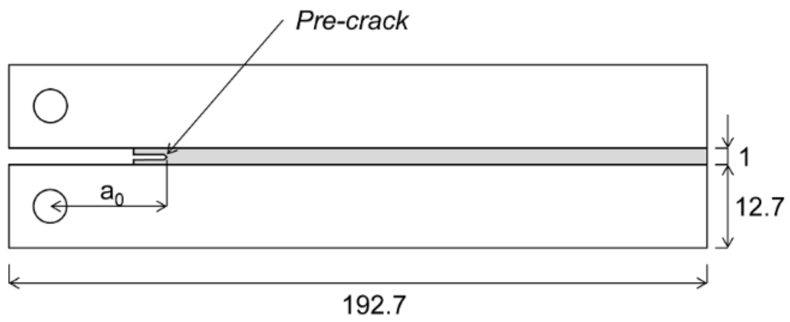

Figure 5 - DCB specimen geometry (dimensions in mm)

Several methods have been developed to obtain the fracture energy value from the DCB test data. Most require the constant monitoring of the crack tip position, to correlate the crack advance with the load level. This, however, poses significant problems as it is very hard to measure the actual crack tip location and does not take into account the presence of a fracture process zone (FPZ) immediately ahead of the crack tip. Additionally, if a DCB test is done inside a thermally controlled chamber, it becomes especially difficult to measure the crack progression. Therefore, a method that does not require crack length measurement was employed in this work, the Compliance-Based Beam Method (CBBM). This method was proposed by de Moura et al [21-23], and does not require information regarding the crack tip location. Instead it uses the crack equivalent concept, which is dependent only on the specimen's compliance, obtained directly from the testing data. The GI_c equation uses an estimated crack tip location calculated from the Castigliano beam deflection theorem, with a correction needed due to the initial crack length. By using the experimental data and the measured initial compliance of the DCB specimen, this formula takes into account the experimental compliance and the FPZ at the crack tip, removing any variability introduced from crack measurement procedures.

3.3 Glass transition temperature (T_g) measurement

The T_g of an adhesive is an extremely important parameter to understand its behaviour when subjected to large temperature gradients. This property allows to determine if the adhesive is going to have a brittle or flexible behaviour at a given temperature and therefore, if it's prone to failure or flexible enough to handle any deformation.

During the course of this thesis significant work time was devoted to the development and improvement of an apparatus to measure the T_g. This apparatus is based on the work by Zhang et al. [24] and it finds the T_g by measuring changes in the damping properties of the adhesive. At T_g there is a significant increase in the damping of the material. The apparatus works by keeping a beam containing an adhesive sample vibrating at the resonance frequency and gradually varying the temperature. When the T_g is reached, the damping of the adhesive sample rises significantly and the amplitude of the beam's vibration is almost reduced to zero. Figure 6 shows the main components of this device.

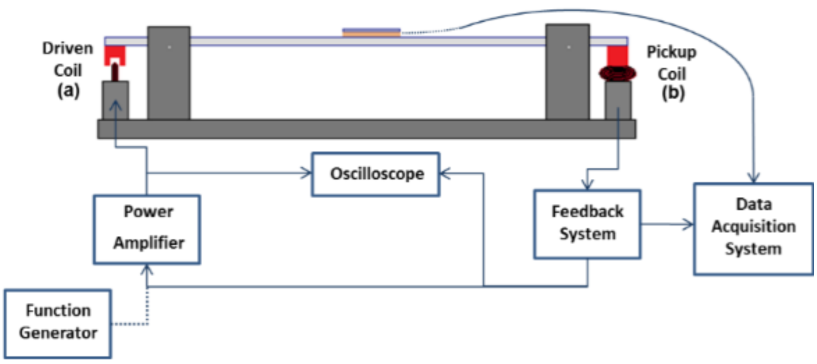

Figure 6 - Schematic representation of the T_g measurement apparatus

3.4 Ceramic bulk testing

The properties of ceramic materials are usually very difficult to accurately determine. Although there are various standards available for testing ceramics [25], the properties obtained with these standardized methods are hard to correlate with the properties necessary for use in finite element models, especially if cohesive zone models are to be used. Therefore, for this work, an inverse method was employed.

The ceramic block used in the joints described in this work is loaded mainly in a shear mode. A novel specimen type was designed using finite element analysis, in such a way as to load a thin central section under a pure shear loading (Figure 7). The dimensions were carefully tuned to ensure that the loading was as close to pure shear as possible and the specimen was precisely produced using water jet cutting. This specimen was then tested and the results were correlated with those of a finite element model with the same dimensions of the experimental specimen. The finite element model contained a cohesive element layer at the central section. The cohesive properties were then selected to ensure a good match between the experimental and numerical model.

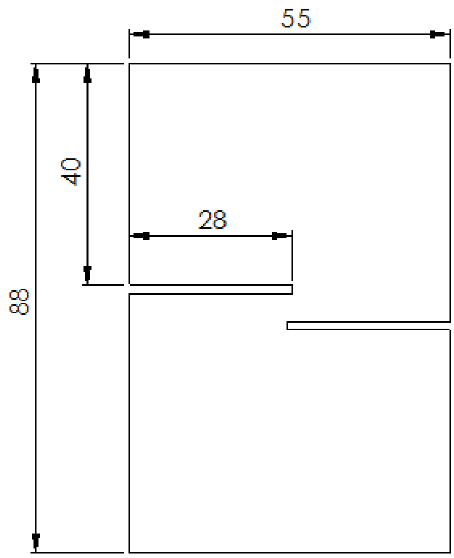

Figure 7 - Ceramic bulk testing specimen geometry (dimensions in mm)

3.5 Single lap joints (SLJ)

As part of the characterization process of the RTV106 adhesive, tests were made to assess the adhesive strength in SLJ specimens. The SLJ specimens follow standards ASTM D1002-99 [26] and ISO 4587:1995 [27]. From the experimental load-displacement curves maximum loads were obtained. Figure 8 shows the geometry of the SLJ specimens used in this work.

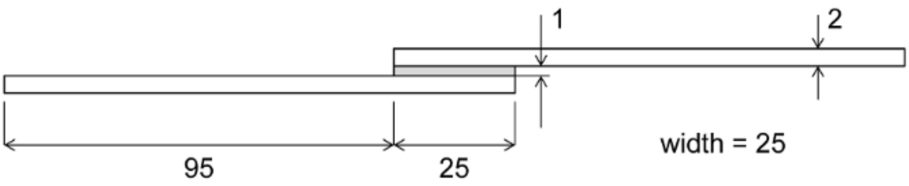

Figure 8- Typical single lap joint geometry (dimensions in mm)

3.6 Complete joint testing (static)

To test the actual mechanical behaviour of the dual adhesive joint under various conditions, a special testing tool was custom made, allowing the specimen to be tested in a universal testing machine. This tool fixes the metal-ceramic specimen in position and subjects it to a shearing load, by pulling the ceramic tile away from the metal panel. Figure 9 shows this tool and its main components.

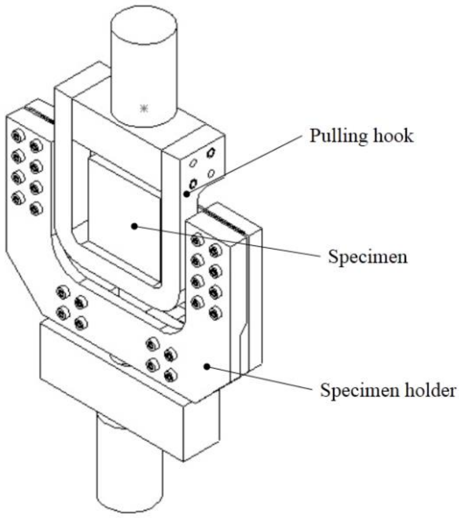

Figure 9-Schematic representation of the static testing tool and specimen

The specimen is fastened between the two parts of the specimen holder, which are rigidly fixed to the static part of the testing machine. Surrounding the specimen is a hook shaped part, rigidly connected to the moving crosshead of the testing machine. The movement of the crosshead is directly transmitted to the ceramic tile, which is then gradually sheared away from the metal substrate.

This tool is used to perform tests not only at room temperature but also at high (100ºC) and low (-65ºC) temperatures.

For high temperature testing, heat was applied locally to the ceramic tile face using a gas burner. This procedure was calibrated using thermocouples embedded in the adhesive layer as a way to ensure that the temperature inside the specimen is consistently around 100ºC during the mechanical testing. For the low temperature testing phase, the full setup was subjected to the low temperature by encasing it with a styrofoam insulating case and introducing dry ice (CO_2) pellets to cool the interior of the box. The specimen temperature gradually reduced and when the testing temperature was reached the test was performed.

The relative complexity and size of this testing tool meant that during testing it introduced an extra displacement in addition to the displacement of the tested joint. To allow the comparison of the experimental results with numerical results, this extra displacement had to be quantified and removed from the experimental data. For this purpose, an experimental procedure was devised where a dummy steel specimen, of negligible deformation was loaded using this tool. The resultant load displacement curve of the dummy specimen was then subtracted from the experimental load-displacement curves of the adhesive specimens, therefore removing the influence of the testing tool.

3.7 Complete joint testing (impact)

Due to high energies and the materials involved, impact loads can have significant effects on the strength of adhesive joints The behaviour of an adhesive subjected to impact can exhibit high strain rate dependency, turning an adhesive which is a non-brittle adhesive under static or quasi-static conditions into a brittle adhesive when a dynamic load is applied. This consequently affects the capability of energy absorption of the joint [28]. Impact testing was added to this work in order the study the effect of this particular type of loads in dual adhesive joints. For this purpose, a drop weight testing machine was employed. This machine drops a weight on the specimen, which is fixed in an anvil, as shown in Figure 10. Again, due to the particular shape of the specimen, a special holding tool was developed, quite similar in concept and construction to the tool presented in the previous section regarding static testing. All the impact tests were performed at room temperature and used a hammer with 25 kg and a testing speed of 4 m/s.

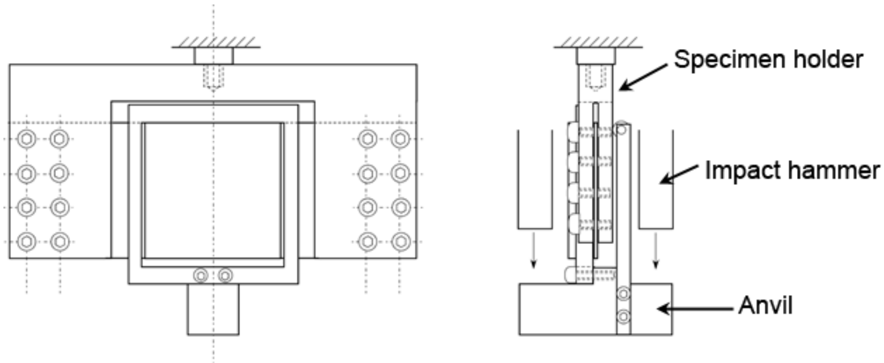

Figure 10- Schematic representation of specimen holder, impact hammer and anvil used for impact tests.

4 Numerical modelling

Numerical modelling was employed in this work, mainly in **Papers 5** and **Paper 6**, with the aim of validating mechanical properties, develop a strength prediction method and finally as tool to improve and optimize the dual adhesive joint geometry.

4.1 Cohesive zone models

To correctly simulate the failure mode and failure loads of the experimental joints, the finite element models were developed making use of cohesive type elements. These elements use a cohesive zone model (CZM). This type of models is increasingly being used to improve the failure load prediction of finite element models (FEM). Needleman [29], Tvergaard et al. [30] and Camacho et al. [31] have proven the suitability of this technique for use in modelling adhesive joints. A CZM is able to represent the fracture process and location, advancing beyond the typical continuum mechanics modelling. It does this by including in the model a series of discontinuities modelled by cohesive elements, which use both strength and energy parameters to simulate the nucleation and advance of a fracture crack [32, 33]. Cohesive models use fracture mechanic concepts, combining strength and energy parameters to simulate a crack progression on the material.

For this thesis, the commercial FEM package Dassault Systèmes ABAQUS® (Vélizy-Villacoublay, France) was used and the numerical analysis were performed in two and three-dimensional models. Cohesive elements were introduced in the model where the failure was expected. Figure 11 shows an example of the location of cohesive element layers.

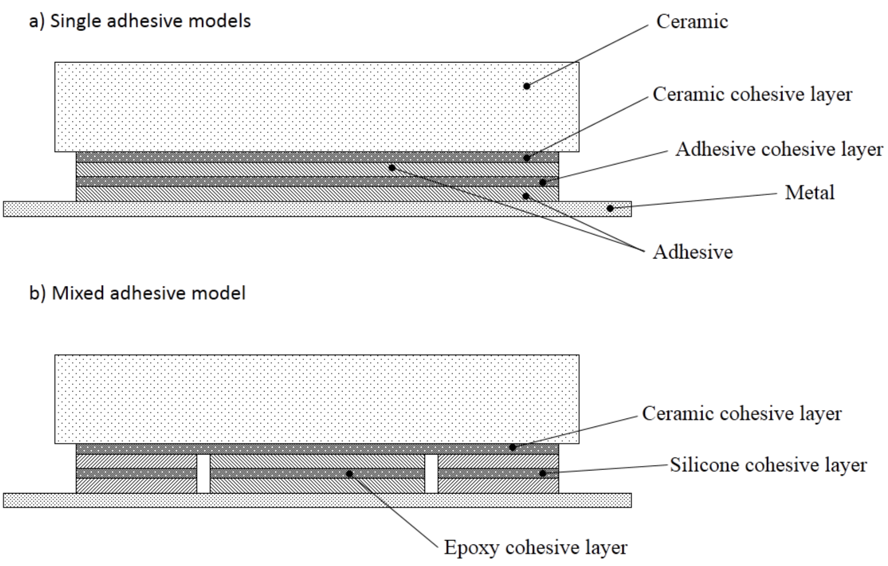

Figure 11- Example of location of cohesive elements in a finite element model.

The joints shown in the figure have two types of cohesive elements. In the upper part of the joints a layer of cohesive elements is applied to simulate possible failure of the ceramic tile right at the interface. Another layer of cohesive elements is located at the middle of the adhesive layers, intended to simulate a purely cohesive failure of the adhesive. In the case of joints with two different adhesives in one layer (Figure 11b – mixed adhesive joint) the cohesive layers for each adhesive must be separated by a small free space, which allows independent evolution of crack progression.

4.2 Determination of cohesive parameters

The CZM natively integrated in ABAQUS® and used in this work makes use of triangular traction separation laws. This type of law can be modelled with three main parameters for each type of loading mode which are then combined internally by the software according to a user specified mixed mode law [34]. Using a triangular traction separation law, the three properties required for each mode (mode I and mode II) are the elastic modulus, the yield stress and the fracture energy. Figure 12 shows the graphical representation of the mode I traction separation law for both adhesives studied in this thesis.

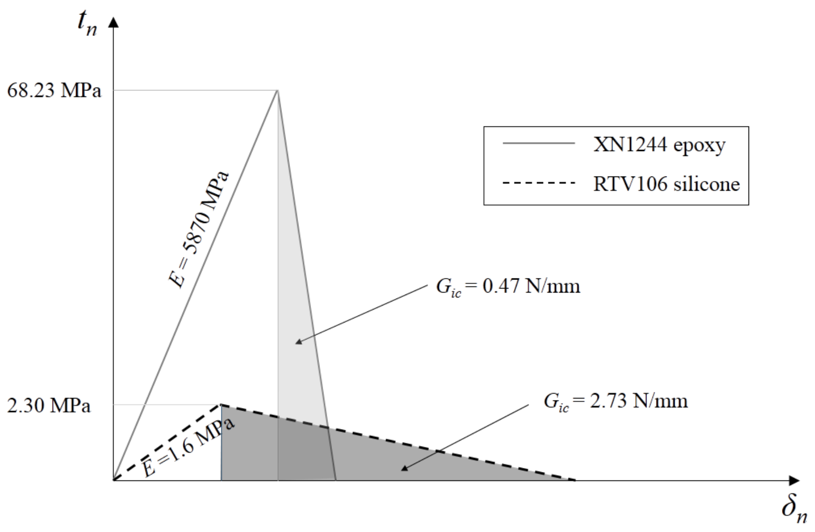

Figure 12- Mode I traction separation laws for XN1244 epoxy and RTV106 silicone

Areas under traction-separation law in each mode are representative of the fracture energy. If the model is operating under a pure mode loading, damage propagation will occur when the stress level reaches the maximum allowed by the relevant traction separation law. If the model is subjected to a mixed mode loading, an energetic criteria must be used to combine the traction and shear, more accurately simulating the mixed behaviour present in the adhesive joint layer.

The cohesive properties parameters can be estimated using various methods, such as the property determination technique and the inverse method.

The property determination technique consists in the step by step definition of each cohesive parameter by the adequate experimental tests. The previously described bulk and DCB tests are among the tests available for this purpose. There are however some differences between the behaviour of the adhesive in a specimen and in a joint. This is fundamentally caused by the differences between the thin adhesive layers in actual joints and the usually thicker specimens. The method to obtain cohesive properties can be found in **Paper 2** of this work.

The inverse method is an alternative method that does not require the complete knowledge of each of the cohesive properties. Here, the results of a numerical model with assumed material cohesive properties (selected to be as similar to the expect properties of the material) are compared with the results from experimental data of the same joint or specimen. An iterative process follows, where the assumed properties of the numerical model are gradually changed until there is good agreement between experimental and numerical data. This method was employed in this work in Paper 5.

5 Conclusions

Despite varied and wide ranging objectives, this work can be understood as a thorough study of the dual adhesive metal ceramic joints, assessing various important aspects such as the feasibility, thermal resistance and impact strength. In an initial phase of this work, published data was studied and used to create a solid base of knowledge to build improvements on.

Well established and standardized testing methods were employed to obtain mechanical property data which complemented the data available in the literature. A reliable and controlled manufacturing technique for ceramic-metal adhesive joints with mixed adhesive layers was developed.

A suitable testing procedure and the necessary tools for this ceramic-metal joints were developed to ensure accuracy in the results. The testing procedure was further developed to allow high and low temperature testing. The ceramic-metal specimens were quasi-statically tested in a wide range temperatures and important conclusions regarding the properties of the mixed adhesive joints were drawn from the experimental data.

Following the static tests, an impact testing procedure was devised and performed. The impact testing performed at room temperatures allowed the understanding of the mixed adhesive joint behaviour under impact loadings, which is important to assess the durability of the joints under extreme loading conditions.

The last steps of the work consisted of a numerical modelling effort, with the aim of understanding not only the more suitable modelling techniques for this type of joint, but also to explore the influence of several important geometrical parameters on the joint behaviour. Good agreement was found between experimental and numerical data, indicating that both the properties and the modelling techniques were adequate for modelling mixed adhesive joints.

As a final remark, it can be said that the explored techniques and procedures are at a maturity level that can be effectively employed to design mixed and high temperature joints suitable for real-world applications.

6 Future work

This work experimentally and numerically evaluated a ceramic metal joint for use in large temperature ranges, suggesting improvements and changes to enhance the overall joint strength. However, further testing and optimization could still lead to more improvements. A possible next step would consist in performing impact tests at high and low temperatures, verifying the correlation between static loads and impact loads at these temperature levels. Other improvements could focus on the materials used. The thermal protection system joint designs presented in this work are flexible and lend themselves to the use of different materials for the insulation, base plate or adhesives. The use of a composite skin instead of the aluminium sheet could potentially be better suited for real world applications, due to the inherent higher strength to weight ratio of composites and their increasingly higher relevance in aerospace structural applications.

Another promising technique that might improve this type of joint could be the use of a graded adhesive joint. Instead of the discrete use of two adhesives in a layer, there is the possibility to vary the adhesive properties locally in such a way as to select the most desirable properties for each point of the adhesive layer. This has already been experimentally proven but not for the temperature ranges of this application, therefore representing an unexplored research area that might yield significant improvements.

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Literature review

Adhesive joints for low and high temperature use: An overview

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Abstract

This work presents a review of several investigations on the topic of adhesive bonding at high and low temperatures. Durability and strength at extreme temperatures has always been a major limitation of adhesives which, given their polymeric nature, exhibit substantial degradation at temperatures where other structural materials (such as metals for example) have minute changes in mechanical properties. However, due to the inherent advantages of bonding, there is a large and continued effort aiming to improve the temperature resistance of adhesive joints and this effort has been spread among the various topics that are discussed in this review. These topics include adhesive shrinkage and thermal expansion, adhesive properties, joint geometry optimization and design techniques, among others. The findings of these research efforts have all found use in practical applications, helping to solve complex problems in a variety of high tech industries where there is a constant need to produce light and strong components that can withstand large temperature gradients. Therefore, the final sections of this work include a discussion on two specific application areas that demonstrate the strict demands that extreme temperature use imposes on adhesive joints and the methods used to improve their performance.

Keywords: High-temperature adhesives; Low-temperature adhesives; Adhesive shrinkage; Thermal expansion; Viscoelasticity; Numerical modelling;

1 Introduction

Adhesive bonding is a technique in which an adhesive is used to join two substrates together. Adhesive joints are known to have some significant advantages when compared to other joining techniques such as fastening or welding [1, 2]. Adhesive joints exhibit a very smooth stress distribution which translates into better fatigue resistance, they are light, relatively cheap to manufacture and can exhibit a large tolerance to damage [3]. They are also able to effectively join dissimilar materials, which is a capability of particular importance to the high temperature usage discussed in the course of this work. The use of adhesive joints is now relatively widespread having increased steadily during the 20th century. While initially limited to low strength applications, advances in the chemical industry and research have led to the formulation of improved adhesives that enabled bonding to be a valid solution for structural joining applications. Adhesives are now in use in a wide variety of industries, such as automotive, aerospace, electronics and naval [4]. Some of these industries manufacture products that are expected to perform adequately under a large range of environmental conditions, of which the temperature variation is one of the most common and, arguably, one of the most important parameters. Therefore, there is a substantial demand for the development of adhesive joints and adhesives able to withstand large temperature gradients. This is a considerable challenge, as structural adhesives are almost all polymer-based and therefore have a relatively low capability to withstand high temperatures. However, the combination of recent advances both in adhesive chemistry and joint design techniques have allowed the development of adhesive joints optimized for extreme temperature. A variety of adhesives specially designed for this purpose is currently commercially available. Room temperature vulcanizing silicones, high temperature epoxies and even ceramic based adhesives can be used to bond structures intended to be used in large temperature ranges.

Regarding joint design, there is a large amount of work in optimizing the joint geometry to effectively deal with the stresses generated by thermal loads. The investigations in the field of joint design range from simple improvements, such as the careful selection of substrates to minimize differentials in the thermal expansion to significantly more complex techniques like the combination of two different types of adhesives in a single joint or even the use of graded adhesives, where the properties of the adhesive are not constant along the overlap length. Numerical modelling techniques are also an important research field that aims to simplify the joint design process, allowing the accurate prediction of failure loads by taking into account the variation of mechanical properties with temperature, the evolution of thermal loads and the associated thermal stresses that appear in the adhesive layer [5].

This review is divided in various sections, each discussing a topic related to adhesive use in extreme temperatures. The first sections describe the stresses that appear in adhesive layers caused by shrinkage and the differential thermal expansion of materials. A discussion about viscoelastic effects is followed by a description of adhesives suited for high and low temperatures and their properties. Next, a section regarding the design of joints for these thermal conditions is also presented, with the improvements brought by each type of joint geometry compared. This section also includes advances in modelling and in predicting the strength of these joints. To finish, practical application examples are given, explaining the particular demands of each application and the techniques and materials used to solve the particular problem. Finally, future trends are listed

2 Adhesive shrinkage

While designing and manufacturing an adhesive joint, especially if might be subjected to thermal stresses, one must be aware of the fact that hot-cure adhesives exhibit a shrinkage in volume while cooling from curing temperature to ambient temperature. Shrinkage of the adhesive layer is a consequence of the polymer shrinkage that occurs during cure. The amount of shrinkage depends on the adhesives chemical structures and the types of attractive forces that appear and disappear as the adhesive cures. Watts et al [6] describe the case of di-methacrylates where during curing, the *van der Walls* force and a C=C double bond are replaced with a pair of single covalent bonds, which reduce the free space in the adhesive. It is also known that the cure contraction can sometimes be reduced by the introduction of inert fillers in the adhesive bulk [7].

Yu et al [8] have developed a device intended to accurately measure this shrinkage at various curing temperatures, shown in Figure 1. Shrinkage of 5% in volume was found for epoxy adhesives, while acrylics were found to shrink up to 15%. The volume shrinkage was also found to be divided in two distinct phases, as there is different shrinkage before gelation and after gelation. While most of the shrinkage happens in this phase before gelation, it has been determined that around one third of the shrinkage occurs after gelation and therefore is able to introduce internal stresses in the adhesive. It was also found that reducing the curing temperature resulted in reduced shrinkage.

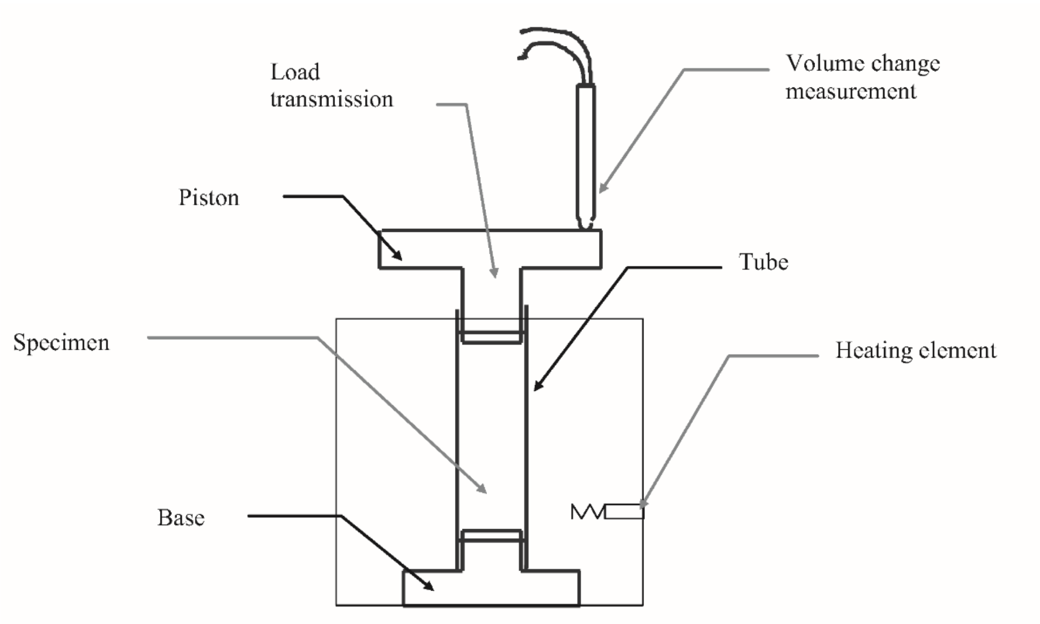

Figure 1- Schematic drawing of the shrinkage measurement apparatus [8]

Lu and Wong [9] measured the shrinkage of conductive epoxy adhesives with a thermo-mechanical analyser (TMA) and found volume changes between 2.98 and 4.33%. Hudson et al [10] used a novel optical method to measure the shrinkage of UV cured adhesives. They found shrinkage of 8.7%. Zhang et al [11] used a force based method to measure the shrinkage of non-conductive adhesives for electronics packaging. This method suspends an adhesive droplet between two glass rods. The adhesive is then cured and the force exerted in the glass rods is registered. This allows the calculation of the shrinkage, which was found to be 4.29% for the studied adhesive.

Adhesives that cure at room temperature by various methods, such as water absorption, might have even smaller shrinkage values. Room temperature vulcanizing (RTV) silicones exhibit linear shrinkage between the 0.5 and 1%.

Coppendale [12], using a two dimensional finite element analysis, demonstrated that for the failure loads of the single lap joints studied (between 10 kN and 20 kN), the contribution of the shrinkage to the strain is very small, around 0.5%. This led to the conclusion that for lap joints, there is no necessity to account for shrinkage. Other works focused in the comparison with thermal stresses. Mallick [13] studied the stresses in single lap joints bonding carbon fibre reinforced plastic (CFRP) to aluminium. The stresses introduced by the shrinkage were compared with the stresses caused by a temperature reduction of 150ºC and a 5 kN loading. The adhesive shrinkage was again found to have a very small contribution for the total stress state of the adhesive joint. Yu [14] demonstrated that when coating a metallic strip with an adhesive layer, the stresses caused by the difference in the thermal expansion coefficients overwhelmed the shrinkage induced stresses. This was again confirmed by Yu et al [15], by experimentally testing an epoxy-steel laminate. Some authors have developed constitutive models able to capture the stresses generated by crosslinking polymers. The work of Adolf and Martin [16] and Adolf and Chambers [17] allows the calculation of internal stresses in thermo- and chemorheologically simple polymers and for time-dependent strains where the total strain is sufficiently small that linear viscoelasticity applies.

It can be concluded that most hot-cure adhesives, like epoxies, exhibit reduced shrinkage during curing while adhesives that cure by other methods such as water absorption, have almost no shrinkage. The stresses generated by shrinkage are relatively small and researchers found that their values were not as significant as those generated by other phenomena, such as differential thermal expansion. However, strains generated during adhesive cure can still induce distortions post-cure in finished products and in many cases must be carefully controlled and its effects mitigated.

3 Differential thermal expansion

As demonstrated by the publications cited in the previous section, while the stresses induced by adhesive shrinkage are of reduced magnitude, thermal expansion induced stresses are significantly stronger and their reduction is an extremely important task for anyone who designs an adhesive joint. The thermal expansion stresses can be of great importance not only when the adhesive joint is in service but also during the cooling phase from curing temperature. A large number of studies on the influence of thermal stresses in various types of adhesive joints are available [18, 19, 20, 21, 22, 23, 24]. Lee and Lee [18] introduced a model for tubular lap joints incorporating the magnitude of the residual thermal stresses induced by the fabrication process. Reedy and Guess [19] studied the cooling stresses in a butt joint and found that the adhesive displayed highly nonlinear, stress level-dependent viscoelasticity at stress levels approaching the adhesive's yield strength, and significant stress relaxation occurs once the adhesive yields, demonstrating that a linear analysis could not accurately be used to calculate stress levels. Kim et al [20, 21] studied the stresses in a tubular adhesively bonded joint, proposing a non-linear adhesive failure model with thermal residual stresses due to manufacturing. Cho et al [22] focused on the effect of curing temperature in polyimide-copper joints. In these very dissimilar materials, the adhesion strength was found to fall proportionally to the increase in curing temperature and curing time. Nakano et al [23] studied butt joints with circular holes and rigid fillers. A parametric study on the location of these fillers and holes demonstrated that the thermal stresses could be controlled. Nagakawa [24] further numerically investigated this type of joint with hole type defects, finding that the stresses around the hole were larger near the centre of the adhesive that at those located in the free surface of the adhesive.

The coefficients of thermal expansion (CTE) that lead to the stresses introduced in all these publications can be experimentally determined by dilatometry [25], using strain gauges, or using a bi-material curved beam method [26]. As shown in Table 1, the CTEs can differ between different types of adhesives and substrates and for some combinations leads to considerable expansion differentials

Table 1 - Typical coefficients of thermal expansion (CTE) of various adherends and adhesives

Material	**CTE ($x10^{-6}$ $^oC^{-1}$)**	
Aluminium	24	
Steel	12	
Titanium	9	
Glass fibre	6	
Carbon fibre (axial)	-0.5	
Carbon fibre (radial)	10	
Carbon fibre reinforced epoxy (longitudinal)	-0.1	
Carbon fibre reinforced epoxy (transverse)	30	
	Below T_g	Above T_g
Epoxy	60	180
Bismaleimide	35	114
Polymethyl metacrylate	26	53

Large stresses caused by this differential can therefore appear in the substrates and in the adhesive layer. In the case of a single lap joint bonding composite to metal, during cooling from cure temperature, the metal shrinks while the composite, with much lower CTE does not present a significant change. If a flexible adhesive is used, the adherends can contract freely and no significant stresses arise in the joint. However, when the adhesive is stiff, such as an epoxy, the difference in length between the dissimilar adherends is not easily handled by the adhesive, leaving the composite under a compressive load and the metal subjected to a tension load. This leads to bending of the joint and the stress field in the joint will be composed of the uniform axial load plus a new bending component [27]. Figure 2 shows four different cases, depicting the relative deformations of a joint when cooled from a given temperature. The cases show, with various combinations of adhesives stiffness, the loads acting on the joint.

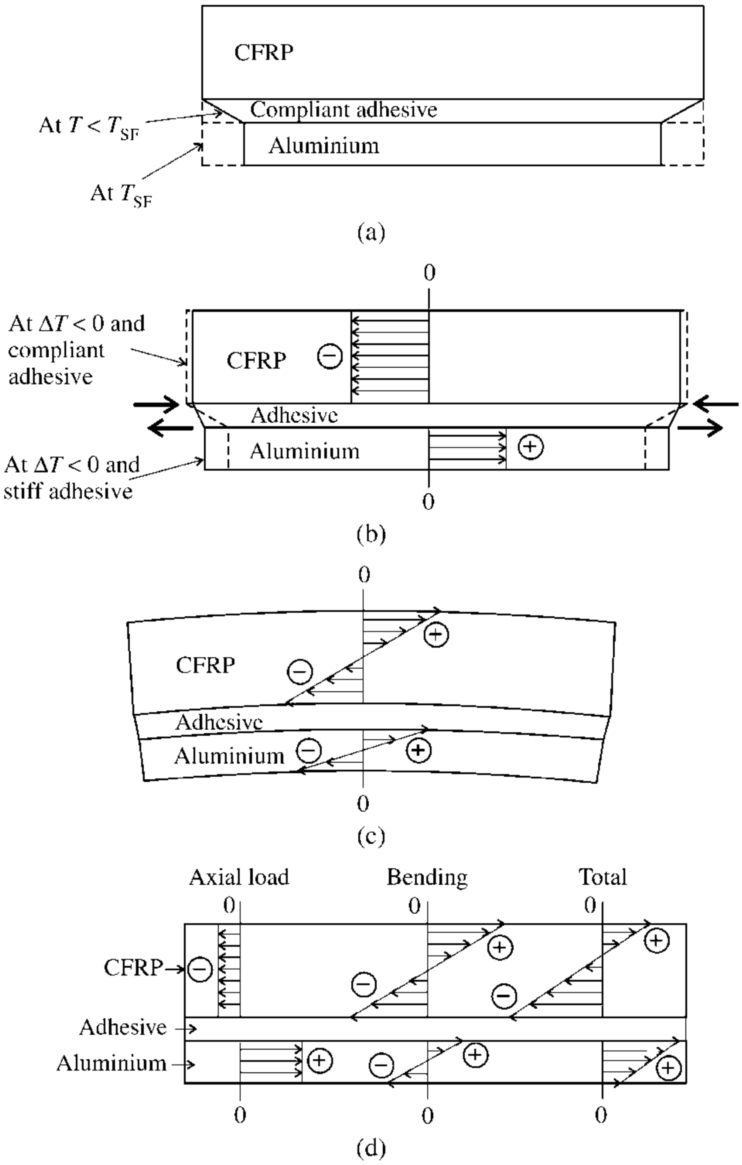

Figure 2*- Stresses in adherends for various cases. (a) negative thermal load (ΔT<0) and a compliant adhesive; (b) for ΔT<0 and a stiff adhesive, axial component; (c) for ΔT<0 and a stiff adhesive, bending component; (d) for ΔT<0 and a stiff adhesive, axial plus bending components [27].*

The relative magnitude of these two components is strongly dependent on the joint geometry and material properties. The magnitude of the thermal load in an adhesive layer can be evaluated by the thermal load (ΔT) equation:

$$\Delta T = T_O - T_{SF} \tag{1}$$

Where T_O is the operating temperature of the adhesive and T_{SF} is the stress free temperature. The concept of the stress free temperature of an adhesive was introduced in 1973 by Hart-Smith [28] and corresponds to the cure initiation temperature, which is slightly below actual the cure temperature of the adhesive. However, due to the small difference between the cure initiation temperature and the cure temperature it is common and acceptable to assume T_{SF} as being the cure temperature.

This simple relationship is however limited, as it is only valid if the adhesive is operating below the glass transition temperature (T_g). At temperatures above T_g, the adhesive abandons the glassy phase and enters the rubbery phase. This leads to improved flexibility and much less susceptibility to accumulation of stresses [14, 29]. However, when the adhesive is cooled back to temperatures below T_g, there is again a build-up of stresses. Therefore, the T_{SF} is discarded as the reference point and the T_g, value should be used in its place. This relation between T_g and T_{SF} was experimentally proven by da Silva and Adams [25]

In summary, the presence of thermal stresses generated by differential thermal expansion is known to be one of the most significant challenges faced by the use of structural adhesives in large thermal gradients. Joints comprised of stiff adhesives bonding metal or composite substrates have high levels of thermal stresses. However, adhesives which are cured and operate always above their T_g are almost unsusceptible to the appearance of thermal stresses. There is an exception however when soft adhesives are placed in very thin bondlines with large bonding areas. In this case, the large area and the reduced freedom in the thickness direction can cause large stresses even with very flexible adhesives. Adhesives, substrates and joint geometry therefore must be carefully selected to minimize these effects and avoid premature joint failure.

4 Viscoelasticity

Polymer based adhesives are known to exhibit time dependent stress-strain behaviour under static loads, due to their viscoelastic properties. This is commonly translated into creep, a reversible joint deformation that occurs at load values below the yield strength of the adhesive [30]. The strong time dependency and non-linear behaviour of this phenomenon can cause problems in determining and predicting the long term strength of an adhesive joint. Thermal loads are a very important factor in the evolution of creep deformation and therefore introduce further challenges in the prediction of joint strength [31].

To design a joint intended to operate under sustained load at high temperatures, a good knowledge of the adhesive's creep behaviour is required as well as a suitable prediction model. In 1982, Peretz and Weitsman [32] undertook one of the earliest studies on the creep of adhesives. They characterized the thermo-elastic behaviour of a rubber toughened epoxy film adhesive. The creep tests were carried at different temperature and stress levels. They found that at 70ºC the coupons exhibit premature rupture due to creep. They also identified that at certain stress levels the creep rate was directly proportional to the temperature increase. In 1985, Jurf and Vinson [33] did similar work for an epoxy adhesive film but also included the effect of moisture. They found that moisture and temperature had similar and very damaging effects in the creep behaviour of an adhesive joint. Polymeric materials exhibit linear viscoelastic behaviour at low stresses, usually defined as those with a corresponding strain below 0.5% [34].

To simulate the creep behaviour of adhesives, two different elements are commonly used. A spring element is used to represent the mechanical elastic portion of the behaviour while dashpot elements are used to simulate the linear viscous flow. Maxwell introduced this approach with a simple model containing only one spring and one dashpot, roughly approximating the viscoelastic behaviour of a material [35]. However, more complex models have been devised with a large or even infinite amount of elements interconnected. The greater the number of elements used the better the model can fit the behaviour of actual adhesives. Temperature can be introduced in the study of viscoelasticity using the time-temperature superposition principle. This principle assumes that that in the linear viscoelastic region, there is a similarity between time dependency and temperature dependency. Using this principle, the change in an adhesive property caused by a certain amount of time can be directly related to the change in that property caused by a certain increase in temperature. The viscoelastic behaviour of an adhesive can be obtained using a dynamical mechanical analysis at a range of different temperatures, using it to create a master curve of temperature-dependent data. Ferry et al proposed a function that allows to extrapolate these properties to temperatures outside of the experimentally tested range [31].

As mentioned previously, the time-temperature superposition principle is only valid for linear behaviour. In joints used in practical applications it is common to have large stresses and elevated temperatures that often lead to non-linear creep behaviour [36]. Polymers are very susceptible to changes in the mechanical properties with temperature due to the high level of molecular mobility found at elevated temperature and for most adhesives, T_g indicates the limit for operating temperature of adhesives. As the T_g is approached, the viscoelastic responses of the material become extremely non-linear introducing the before mentioned difficulties in prediction. This has been demonstrated by Sen et al [37] and O'Connell et al [38].

While constant temperatures can cause damage to adhesive joints, smaller but cyclic changes in temperature can also induce significant thermal stresses in an adhesive joint, changing the mechanical properties of a viscoelastic adhesive. An adhesive joint subjected to thermal cycling can exhibit cracks and fail, with the debonding being caused by the accumulation of thermal stresses induced by CTE mismatch, stresses which would not be able to damage the joint under steady-state thermal loading. Humfeld and Dillard [39] studied this phenomenon and determined that for certain adhesives, the viscoelasticy of the polymers plays a major role. When the temperature of a bond is raised the polymer is subjected to elevated thermal stresses because of

CTE mismatches but the high temperature also allows easier polymer chain mobility and some degree of relaxation of this stresses. However, when the cycling returns the joint to a low temperature, the low stresses at high temperature are converted in an increase of stresses at low temperature. Due to the reduced polymer chain mobility at low temperatures the stresses cannot be relaxed and are therefore locked in. This is repeated for each cycle and leads to accumulation of low temperature stresses, eventually leading to cracking of the material. Hu et al [40] characterized a cyclic-temperature degradation response in two different adhesives. The specimens were subjected to a temperature cycle between -30 and 80ºC. The experimental results were then used to validate a cohesive finite element analysis model that was successfully able to predict the failure load of specimens subjected to thermal cycling.

After an analysis of the research work performed in this area, it can be concluded that adhesive joints subjected to thermal loadings are susceptible to early failure due to creep. There is still difficulty in predicting this phenomenon, especially for adhesives that are operating near their T_g, where there is substantial property non-linearity. Cycling loadings are also an item of concern, as it has been demonstrated that the combination of CTE mismatches and visco-elasticity can lead to an accumulation of thermal stresses. Again, careful material and geometry selection is required, combined with, if possible, experimental tests to anticipate and avoid this type of failure.

5 Adhesives suitable for extreme temperature use and respective properties

As previously referred, most adhesives are polymer based and therefore exhibit some degree of degradation at temperatures above 200ºC. Therefore, the chemical stability of adhesives at high temperatures is one of the major factors that must be taken into account when selecting an adhesive for thermally demanding application. One of the other main defining properties for the suitability of an adhesive for high or low temperature applications is the T_g. At temperatures below the T_g there is high modulus and strength combined with reduced ductility. Above T_g, the opposite is true and the adhesive will be flexible and tough, but with small mechanical strength. Therefore, high temperature adhesives will generally benefit from a high T_g, while adhesives more suited for low temperature use will have a low T_g. As a practical example, a high temperature epoxy might have a T_g near 150ºC and a room temperature vulcanizing silicone, suited for low temperature use, will have a T_g near -65ºC. Table 2 lists typical T_g values for adhesives

Table 2- Typical glass transition values of adhesives

Adhesive	**T_g (ºC)**
Epoxies	
Toughened epoxy	50-150
Epoxy phenolic	200
Epoxy nylon	50
Epoxy polysulfide	50
Phenolics	
Nitrile phenolic	120
Vinyl phenolic	70
Neoprene phenolic	70
High temperature adhesives	
Bismaleimide	210-280
Polyimide	340-430
Stiff Polyurethanes	20-50
Anaerobics	120
Cyanoacrilates	80
Modified acrylics	60-120

5.1 Polyimide adhesives

Polyimides are adhesives that are able to withstand temperatures above 200ºC. They are usually film based, supported by a carrier of nylon, polyester or glass fibre, with glass fibre carriers being the optimal solution for high temperature usage. Most of the research in polyimides was performed by NASA researchers, focusing on the high performance polyimides of the LaRC type [41]. These polyimides, supported by a film carrier, can be used as an adhesive for bonding metals such as titanium, aluminium, copper, brass, and stainless steel. The film carrier performs a very important function in these adhesives as it not only supports the adhesive but also provides bond line control and acts as an escape channel for the volatile reaction products and solvents that are released during the curing process. The curing process for polyimides is complex and to provide the full curing (complete imidization) of the material at low bonding pressures, temperatures near 350ºC might be required. NASA researchers have used lap shear test to study the behaviour of these materials under a variety of conditions including high temperature. St Clair et al [42] performed a series of tests in specimens bonded with LaRC-TPI adhesives. The strength of the specimens was found to vary between 20.7 MPa and 41.4 MPa (3000 to 6000 psi) at room temperature and when subjected to high temperature decreased to values between 13.8 and 20.7 MPa (2000 to 3000 psi). Hergenrother et al [43] tested another type of amorphous polyimide at high temperatures and found that the lap shear strength reached a maximum value of 54.1 MPa (7850 psi) at room temperature and decreased to around 28.3 MPa (4100 psi) at 121ºC.

5.2 Bismaleimide adhesives

Bismaleimide resins (abbreviated BMI), are another class of thermosetting polymers that have good retention of mechanical properties at high temperatures and humidity levels, constant electrical properties over a large range of temperatures and are non-flammable [44]. The highest performing BMI resins are able to withstand extended service at temperatures between 230 and 290ºC, approaching the performance of the best polyimide resins. However, BMI resins alone are known to be quite brittle, due to their high crosslink density. This brittleness has been mitigated in commercially available products by combining BMI with diallylbisphenol A (DABA) [44]. This copolymer maintains all the high temperature performance of the BMI resins but has toughness approaching that exhibited by the best epoxy resins. Compared with polyimides, working with bismaleimide resins is considerable easier, as they do not release volatiles during cure and therefore require less contact pressure to reduce the appearance of voids in the bonding layer.

5.3 Acrylic adhesives

Acrylic adhesives are also a possibility for high temperature bonding. While substituted acrylics like cyanoacrylates are relatively brittle, toughened acrylics might exhibit sufficient mechanical strength for many applications. In acrylics, the polymerization creates a high molecular weight adhesive with a T_g that is independent of cure temperature as the temperature resistance of the polymerized acrylic is determined by the monomers and polymers present before curing and not by cure conditions. Acrylics are usually supplied as pressure sensitive adhesives [45]. The maximum operating temperatures of some systems are usually around 105 °C which corresponds to the T_g of polymethyl methacrylate although prolonged high temperature exposure may cause thermal depolymerisation of these systems. However, acrylics have been formulated to tolerate much higher temperatures, up to and exceeding 149 ° C (300 ° F); these materials often incorporating epoxy chemistries [46]. Lu et al [47] formulated acrylic pressure sensitive adhesives with special crosslinking compounds that were able to remain effective up to 150ºC, due to a significant increase in the T_g.

5.4 Epoxy adhesives

High temperature formulations of epoxy adhesives have recently become available, providing effective strength and ductility at temperatures up to 200ºC, while not requiring a carrier. Banea and da Silva [48] studied single lap joints bonded with an epoxy adhesive at low and high temperatures. The joint strength reduction, using room temperature strength as reference, was found to be 30% for specimens tested at 80ºC and a drop of only 10% was found for specimens tested at -40ºC. This work was followed with the study of another high temperature epoxy formulation [49]. This adhesive was found to have high mechanical strength and stiffness. Bulk traction specimens of the adhesive were tested at room temperature, 100ºC, 125ºC and 150ºC. For a testing rate of 1 mm/minute, it was found that the tensile strength dropped from 68.23 MPa at room temperature to 6.49 MPa at 150ºC. While there is a dramatic reduction in strength at 150ºC, 6.49MPa is still a relatively high value for an adhesive subjected at such temperatures. This drop in strength was also found to follow a linear behaviour. Two additional works focused in the mode I and II behaviour of this epoxy adhesive [50, 51]. In these works it was found that T_g plays a critical role in the fracture behaviour of the adhesive. The value of mode I fracture toughness (G_{Ic}) was found to be relatively insensitive to temperature up to T_g, but above this value there was a large drop in the G_{Ic} value. For mode II, as the temperature rose, a small increase in the mode II fracture toughness was observed but, as described for mode I, after T_g there was a significant drop in the G_{IIc} value. Souza and Reis [52] have tested the thermal behaviour of diglycidyl ether of bisphenol A (DGEBA) based epoxy adhesives. Their research suggested that for this type of adhesives, the maximum service temperature is on average 40ºC lower than the T_g of the adhesive.

5.5 Phenolic adhesives

Phenolic adhesives, composed of phenol formaldehyde resins are among the earliest synthetic resins produced. These adhesives have good adhesion to polar substrates, good mechanical strength, and resistance to burning and good high temperature properties. [46]. While their use is not as widespread as it used to be, phenolic resins became relevant again due to their excellent fire retardant properties and low smoke generation. Combined with carbon fibre, these resins allow the manufacture of composites with extraordinary fire and smoke performance at temperatures greater than 500ºC. These are the properties that make them very suitable as adhesives for high-temperature applications, such as binders for foundry sand moulds. However, phenolic based adhesives are known to have poor toughness. Their structure has a large amount of crosslinking, making them very rigid [53]. Due to this, most of the phenolics used in the aerospace applications consist of a blend between phenolic resin and a nitrile rubber, combining the toughness and oil resistance of the rubber with the chemical stability and heat resistance of the phenolic [46]. These adhesives are usually supplied in film form and can bond metal parts in temperatures ranging from -55º to 260ºC.

5.6 Ceramic adhesives

For even higher temperatures, above 300ºC, ceramic based adhesives are also available as an option. These adhesives are based on inorganic binding compounds, combined with a variety of fillers. The adhesives are available in two-part systems, one part being the binding compound the other being the filler. After mixing, the adhesive paste is applied to the substrates and cured with temperature. The curing process requires temperatures in the range of 260ºC to 1000ºC, which might preclude the use of these adhesives for some temperature sensitive substrates. Bhowmik et al [54] have tested the use of a ceramic adhesive for bonding titanium substrates. The joints were mechanically tested and found to have an acceptable mechanical strength.

While not strictly a high temperature application, Abuhaimed et al [55] used a pressable glass ceramic to successfully bond porcelain dental implants. A composite ceramic material, reaction cured glass has also been used as an adhesive by NASA and Boeing, bonding a carbon base cap to a silicon base [56]. This glassy-ceramic-metal composite is prepared by reacting a mixture of glasses including a porous high silica borosilicate with boron oxide, to prepare a reactive glass frit, which is reacted with one or more of the intermetallic or metallic substances in the group consisting of silicon tetraboride, silicon hexaboride, boron silicides and boron. The intermetallic or metallic additives act as emittance agents and are required in the formation of a multicomponent stable glass. While there is continuous research in this area, the strength of ceramic adhesives is still substantially lower than that of high performance ceramics and is expected to remain so for the foreseeable future. Their use should therefore be limited to applications where extremely high temperatures are present but without significant mechanical loadings, applications such as halogen lamps, high temperature sensors, heaters, igniters, among others.

5.7 Room temperature vulcanizing (RTV) silicone adhesives

While the research effort is mainly focused on high temperature adhesives, there is also a variety of adhesives especially suited for work at below zero temperatures. For many aerospace applications, adhesives might be required to work in temperatures ranging from -60ºC to 200ºC. While adhesives for high temperature can sometimes be employed in these temperature ranges, they are not the most effective solution, as they exhibit high sensitivity to defects and low impact resistance due to their increased brittleness. The common solution is to use adhesives which are still flexible at these temperatures, such as silicones or polyurethanes. Most sealants, such as polysulphides, flexible epoxies, silicones, polyurethanes and toughened acrylics exhibit sufficient flexibility to be used at temperatures up to -30ºC, however, their mechanical strength is very limited when compared with that of structural adhesives and therefore their bond area must be dimensioned accordingly. Room temperature vulcanizing silicones have been available for high and low temperature use since the 1970's [57] and more recently studied by Banea and da Silva [58]. Their work demonstrates that joints using RTV silicones are able to uniformly distribute the stresses and therefore, there is a proportional increase of the joint strength with an increase of the overlap length, something which does not occur for stiffer adhesives. The same authors performed subsequent work in pure mode I loadings of RTV silicone joints [59], and demonstrated that while there was a decrease in fracture toughness with temperature, it was only significant at 200ºC. At room temperature and at 100ºC, the behaviour under mode I loading was very similar, with limited property degradation. Marques et al [60] tested RTV silicones at low temperatures (-65ºC and -100ºC) and found large increases in both the tensile strength and the Young's modulus as the temperature lowers to near T_g (-78ºC). A considerable increase in the mode I crack propagation energy was also found for the same temperature. Figure 3 shows the adhesive stress strain curves for specimens of the RTV adhesive used.

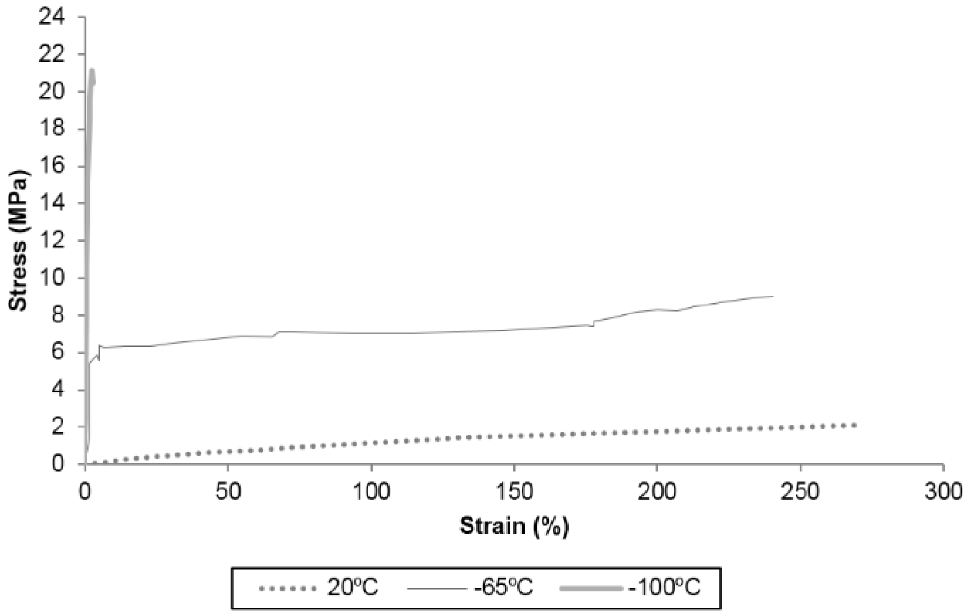

Figure 3- Adhesive stress-strain curves for RTV106 silicone obtained during bulk testing at three different temperatures [60].

While there have been large improvements in the strength of the adhesive under large temperature gradients, the fact remains that the polymeric nature of the majority of the adhesives will not provide good performance at the temperatures that most mechanical fastening methods can sustain. However, the properties of the adhesives are not the only contributing factor for joint strength and behaviour. There still remains the possibility of improving the joint geometry in such a way as to reduce some of the inherent limitations of the adhesives, a topic discussed in the next section of this work.

6 Design of joints for high temperature applications

6.1 Adhesive joint design optimization

Many of the adhesives used for high temperature applications are known to be brittle at low temperatures, while those more suited for low temperatures usually do not provide sufficient strength at high temperatures. To bypass this fundamental incompatibility, the use of dual adhesive joints was first proposed by Raphael [61] as a possible solution. This technique is able to reduce the stress concentration at the ends of the overlap, typical for single lap joints and reduce premature joint failure. The concept entails the introduction of a more flexible adhesive at the ends of the overlap, while a stiff adhesive is used in the central section of the joint, less subjected to deformation during loading. In 1973, Hart-Smith [28] recognized that the use of mixed adhesive joints could yield improvements in mechanical strength for joints subjected in to large temperature gradients. In 2007, da Silva and Adams [62] made use of this concept and predicted improvements in the mechanical behaviour of a joint under a large temperature gradient. In their approach, the adhesives to be combined were not only dissimilar in their mechanical properties, but also in their temperature handling capabilities. The stiffer adhesive was now also a high temperature adhesive (HTA), responsible for the joint strength when the joint is subjected to heat while the more flexible adhesive was now a low temperature adhesive (LTA), carefully selected to be able to provide strength to the joint under negative temperatures. At high temperatures, a high-temperature adhesive (HTA) in the middle of the joint retains the strength and transfers the entire load while a low-temperature adhesive (LTA) is the load bearing component at low-temperatures, making the HTA relatively lightly stressed. At low-temperatures, the load must essentially be supported by the LTA. If its modulus is of the same order as the modulus of the HTA, most of the load will be carried by the LTA. However, if its modulus is much lower than the modulus of the HTA, then there might still be a considerable load in the HTA. Therefore, the geometry and ratios between

LTA and HTA govern the improvement in behaviour over a joint composed only of HTA. Figure 4 shows the working principle of such a joint as well as the stress distributions present in the adhesive layer at two extremes of temperature.

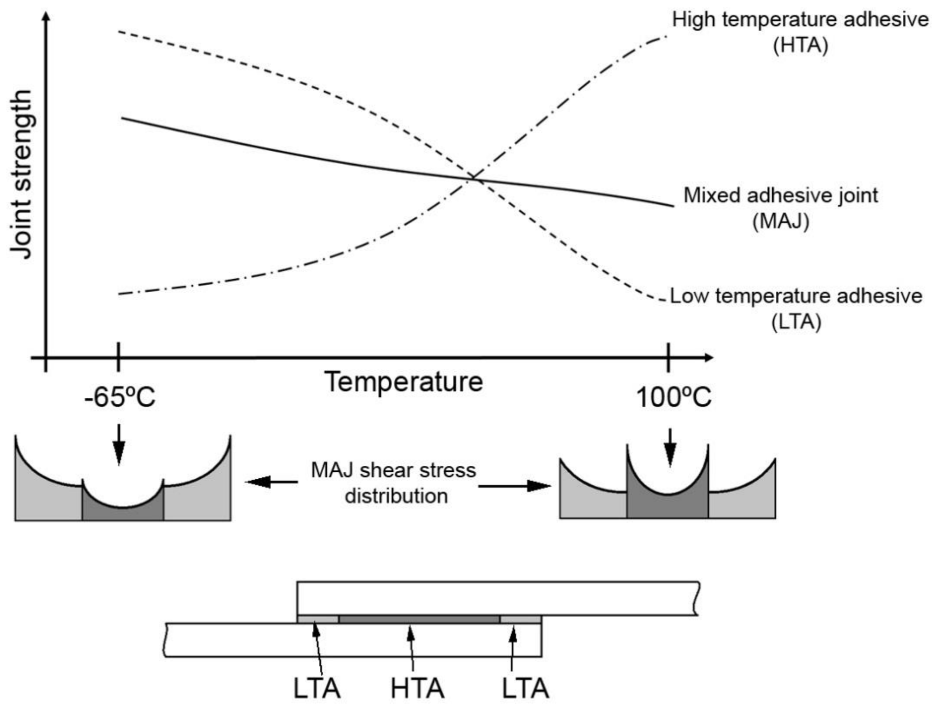

Figure 4 - Mixed adhesive joint concept

It was also demonstrated that this technique is more interesting for practical applications should the adherends be of dissimilar nature. This is mainly due to the volume variation of the substrates under the range of temperatures that the specimen is subjected to. If there is a large disparity in the CTE's, using a single HTA will result in early failure due to the inability of the stiff adhesive to accommodate the thermal expansion differential. By introducing a significant layer of a flexible LTA, the joint can more easily sustain thermal expansion and therefore, should the adhesives be able to withstand it, its temperature range can be expanded. In 2007 [63], da Silva and Adams presented experimental data that supported these conclusions, proving the concept for a temperature range of -50 to 200ºC with titanium and CFRP adherends.

Marques et al [64, 65] performed a series of experimental studies, bonding ceramic tiles to a metallic substrate using a mixed adhesive joint, combining an RTV silicone with a high temperature epoxy. The joints were tested under shear at room temperature, -65ºC and 100ºC. With these static tests, mixed adhesive joints were found to have consistent strength at high and low temperature, while providing a good amount of joint displacement in both cases. Impact tests were also performed and again the mixed adhesive joint was demonstrated as a good alternative to the use of a single adhesive, able to handle large failure loads.

Graded joints have been presented theoretically as the natural evolution of the mixed adhesive joint. They turn the discrete approach of the mixed adhesive joint into a smooth variation of properties that can be obtained via a variety of properties. Theoretical studies have been conducted by Kumar [66] and Kumar and Scanlan, [67] for tubular adhesive joints with a functionally graded bondline, and by Carbas et al., [68] for single lap joints with functionally graded bondline. Kumar [69] studied a continuous (non step-wise) functionally graded adhesive with a step-wise graded equivalent for different adhesive thickness and overlap length in a tubular joint. This study showed that the continuous functionally graded adhesive reduced the shear and peel stresses. Figure 5 shows the working principle of a graded adhesive joint.

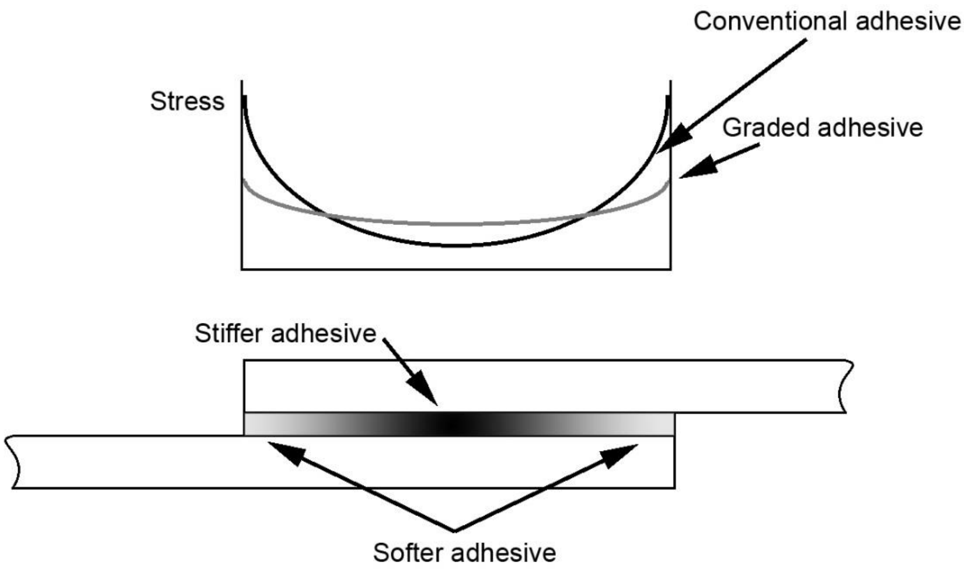

Figure 5- Graded adhesive joint concept

Various techniques have been proposed for the development of such type of joint however, only recently the production of fully graded joints has been experimentally demonstrated and published in literature. Carbas et al. [69] developed an apparatus to provide a differential cure of bonded joints by induction heating. This apparatus of differential cure ensures that the adhesive stiffness varies gradually along the overlap, being maximum in the middle and minimum at the ends of the overlap. The first experimental study of single lap joints with a functionally graded bondline were provided by Carbas et al. [70]. The authors previously characterized the used adhesive as a function of the cure temperature, in order to understand the adhesive behaviour for the different cure temperatures. Functionally graded joints were obtained experimentally by means of induction heating, giving a graded cure of the adhesive along the joint [70, 71, 72]. This study demonstrated that the functionally graded joint shows a good ductility and high strength when compared with joints cured isothermally. The gain in performance of the graded joints is more than 60% in relation to the joints with a homogeneous bondline cured at low or high temperature (brittle or ductile behaviour, respectively). While significant improvements are expected, the strength of this type of joints under temperature gradients remains untested and therefore this technique presents itself as an important and promising investigation path.

6.2 High temperature joint simulation and strength prediction techniques

To accurately simulate the behaviour of an adhesive joint, one must first fully comprehend the temperature distribution of the joint and the relevant physical properties at the service temperatures. Most of the studies found in the literature simplify this step and assume that all parts of the joint are at constant temperature [18, 19, 20, 21, 24, 47, 61, 73 75, 76, 77, 78]. This allows the simple calculation of the thermal stresses induced in the joint if the CTE and stress free temperatures of the adherend are known. The use of additional thermal simulations to investigate the temperature distributions through adhesive joints is a valuable technique to understand the demands on the adhesive layer. This can allow the study of transient conditions and determine the most demanding scenarios. As an example, Marques [64] studied the temperature distribution along a ceramic adhesive aluminium sandwich specimen when a temperature of 1000ºC was applied to the ceramic side of the joint for a given amount of time. Using the F-Chart (Madison, WI, United States of America) Engineering Equation Solver software and an adequate diagram of equivalent thermal resistances the temperature evolution with time was plotted. A scheme of the equivalent thermal resistances used is shown in Figure 6.

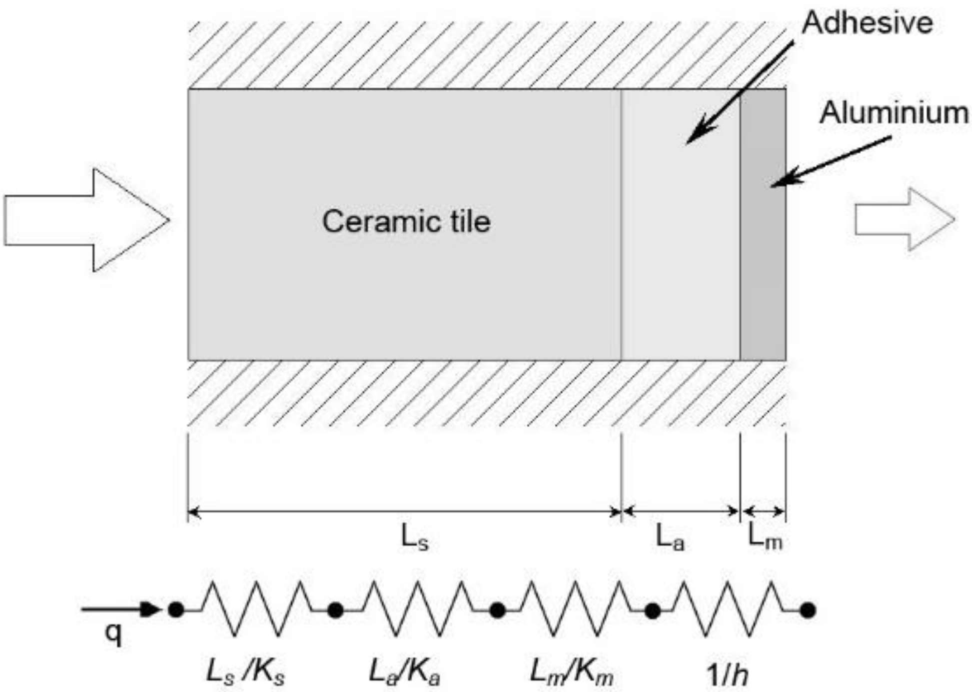

Figure 6 *- Thermal model and thermal resistance diagram for a ceramic-metal adhesive joint. L variables represents the length of each material, K variables represent the thermal conductivity of each material and h represents the convection parameter [64].*

A parametric study found that for that joint the peak temperature in the adhesive could reach 300ºC. Apalak [79] developed a series of analytical models for a variety of adhesive joint geometries that allows the calculation of thermal strains. The author developed a method to calculate the transient temperature of the adhesive layer for a given set of thermal boundary conditions and then made use of the small strain – large displacement theory to solve the system for the calculation of thermal stresses.

With the thermal field characterized, a series of analytical models developed for adhesives can be employed to calculate the stress levels in the joint, including the thermal stresses. These models were presented by Hart-Smith [28], Sinha and Rieddy [80], Adams and Mallick [81], Suhir [82], Rossetos [83], Zhong et al [84] and Wang et al [85]. Cognard et al [86] modelled the behavior of a ductile epoxy adhesive under low temperatures using a 3D elastic plastic model of the Mahnken-Schlimmer type. Using experimental data, they demonstrated that this type of model could accurately represent the temperature dependent behaviour of a ductile adhesive under a proportional monotonic mechanical loads.

In practice, most of the thermal studies of adhesive joints are now performed using finite element analysis. Complex multi-material joint geometries with multiple localized thermal loads pose significant difficulties in the application of analytical models. Finite element analysis usually defines the final temperature in each of the boundaries of the adhesive joint and then uses the material conductivity data to determine the temperature of each point of the model. These temperatures are combined with the CTE free stress temperature and tabled mechanical properties of each material to determine the thermal and mechanical stresses present in the joint.

Cohesive models are increasingly being used to improve the failure load prediction of finite element models. The cohesive zone model is able to represent the fracture process and location, advancing beyond the typical continuum mechanics modelling. It does this by including in the model a series of discontinuities modelled by cohesive elements, which use both strength and energy parameters to simulate the occurrence and advance of a fracture crack [87, 88]. This technique is especially useful for adhesives, as they present a discrete zone, the adhesive layer, where failure can be expected and therefore can be easily modelled. The parameters needed for the simulation can vary as well as the methods used to determine them. In this type of models there is an underlying relationship between the stresses and relative displacements of the nodes of a cohesive element. While initially this type of element has overlapped nodes during the elastic portion of loading, when degradation of the element finally occurs the nodes start to separate and stop providing transmission of load in the model, therefore acting as a real crack in the material. This relationship between the stresses and displacements is governed by a traction separation law, which can be shaped to better suit the behaviour of the material or interface being simulated.

7 Practical application examples

7.1 Automotive industry

Adhesive bonding is a joining technique used extensively in the automotive industry. The need for weight reduction has led to the introduction of multi-material structures, composed not only of steel but also including light metals and composites materials. It has created a need for joining methods able to join these dissimilar materials safely and in a practical and economical way. Adhesive joints are known to be a good solution for covering many of these requirements but their use is not without problems. The thermal loads encountered in the car body manufacture process and during the vehicle service life might pose significant challenges in the design of strong and reliable adhesive joints. During a metallic car body manufacture process, it is in the paint shop that most of the thermal load is induced in the joints. The paint curing ovens can introduce temperatures up to 190ºC during the e-coat phase [89], which are used to help cure the adhesive but are also able to create internal joint stresses due to mismatches of the CTE [90]. This effect is exacerbated if the structure combines multiple types of materials with largely different expansion coefficients, typical of the lightweight techniques currently employed by the automotive industry. Various steps can be taken to mitigate this effect. First, the joint geometry can be optimized to allow the materials some freedom to expand without transferring stresses, which can be done by leaving larger gaps between the substrates or by modifying the adhesive thickness. Some works have found that under temperature, thinner joints are usually stronger and more fatigue resistant [91, 92]. Finite element analysis is a very powerful tool for this optimization process, and can be used to accurately predict the stress levels generated by the thermal loads [79]. The correct selection of adhesives is also an important method to mitigate this problem. By selecting flexible adhesives, able to handle the different levels of thermal expansion, the substrates can be joined without significant transfer of stresses [48, 93]. Lastly, the thermal process itself can also be optimized. By reducing peak temperatures where possible and introducing more gradual heating and cooling phases, the thermal stress build up can be considerably reduced [94].

In fully composite automotive structures, which are only now currently reaching mass production status [95], the paint shop is usually not present and cold curing adhesives are preferred. These materials only face thermal stresses during service, which range from range from -40ºC to 80ºC. For these cases the same thermal stress mitigating techniques previously described apply.

Another example of problems induced by the thermal processes in car body adhesive joints is the bond-line readout defect. The use of adhesive bonding in exterior body panels is very common, as it poses advantages in stiffness, durability and improved sealing. However, if a bondline runs directly underneath the surface of a metal sheet, a surface defect can sometimes be seen after curing. This defect is called bond-line readout (BLRO) and can have various causes. Mechanical BLRO defects are caused by the differences in thermal coefficient of expansion of the substrates and adhesive as well as thermal shrinkage. Figure 7 depicts the type of defects caused by this process.

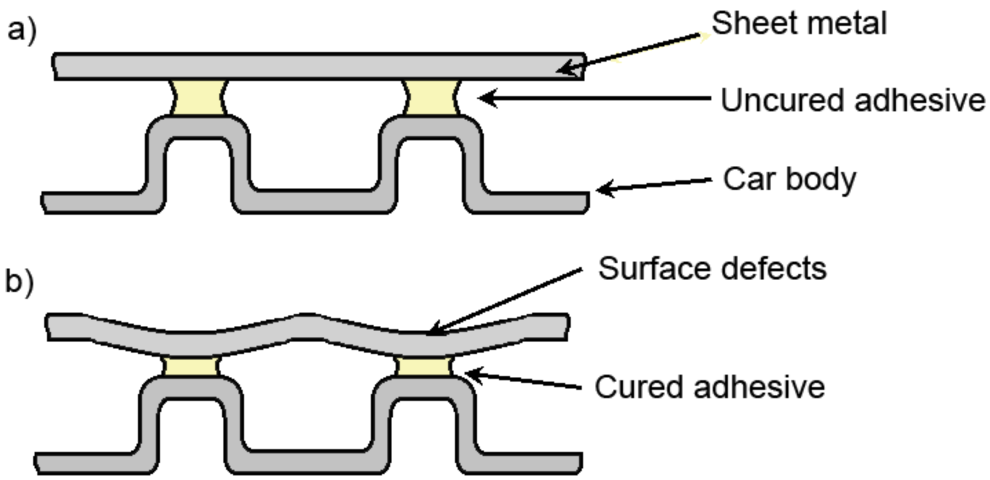

***Figure 7** – Schematic view of bondline defects in automotive structures. a) shows the uncured adhesive under the sheet metal. b) shows the same panel after curing, where the adhesive has shrunk and deformed the sheet metal.*

Eis [96] and Hahn and Jendrny [97] have determined that the curing cycle can induce relative movements of the adherends during bonding. Blanke [98] demonstrated that the geometry and fixture of the curing moulds, as well as the temperature field distribution can be optimized to mitigate this phenomenon. Priesnitz et al [99] studied the influence of the adhesive shrinkage in the distortion of automotive doors after production. They found that the hot-curing one-part epoxy adhesives used for this purpose are responsible for distortions in two different phases. The first phase is the chemical shrinkage, starting as soon as the curing temperature is applied and ending before the cooling begins. The second phase is caused by the thermal contraction of the adhesive. Lower temperature rates in the heating phase were found to reduce the local distortions.

While adhesive bonding is a very powerful joining technique, with significant advantages for car body manufacturing, it must be understood that its use, especially when thermal loads are present, requires an encompassing approach of all steps of the manufacture process, from material selection to procedures.

7.2 Aerospace thermal protection system

One of the most known and studied practical application of the use of adhesives to handle large temperature gradients is the ceramic to metal bond used in the now retired US Space Shuttle program. In this application, over 24 000 individual tiles were individually bonded to the surface of the vehicle. The design of such system was a great engineering challenge, as not only should be reusable and light weight but also extremely reliable. The tiles used initially were made of almost pure silica, combined with a temperature resistant coating [100]. Due to the ceramic construction and large thickness this type of tile is necessarily a heavy component and several upgraded and lighter versions were gradually introduced, adding some alumina content and improved coatings. The tiles were attached to shuttle’s aluminium structure using adhesive bonding but required a strain isolation pad bonded between the tile and the underlying structure. This pad limited the vibration damage and accommodated some of the thermal expansion differential between the tiles [101]. To improve the bonding surface of the tile, a ceramic slurry was applied to the underside of the tile. Gaps between the tiles are required to allow the relative movements caused by thermal expansion of the metallic and ceramic parts. The adhesive used for bonding the tiles is a RTV silicone, suited for high temperature usage. The adhesive is applied and subjected to vacuum pressure to ensure that there are no voids. RTV silicone screed is also spread on the metallic surface before bonding to fill voids and provide a smooth surface for the bonding process [102]. Figure 8 depicts the construction of the shuttle tile attachment and the materials used.

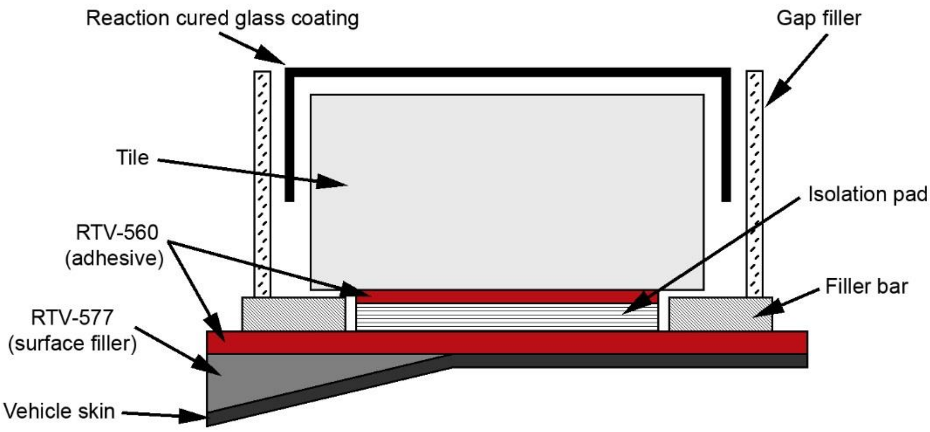

Figure 8 *- Diagram of shuttle tile attachment*

While the space shuttle is now retired out of service, the new generation of thermal protection tiles are still being developed. The new generation tiles, known as TUFROC are manufactured by attaching a ceramic-carbon insulation to a silica based lower block. The two parts of the tile are joined by combining mechanical methods and a high temperature adhesive [103]. The adhesive is reaction cured glass applied in a layer 1.2 mm thick. This material uses glass powders mixed with thickeners and is especially resistant to extremely high temperature and large thermal shocks. It serves not only as an adhesive but also as a non-abrupt transition between thermal gradients. This composite tile can then be attached to a metallic structure using the technique described above for the one-piece tiles. [104, 105]

7.3 Superconducting magnet resin impregnation

The Large Hadron Collider (LHC) installed at European Organization for Nuclear Research (CERN) uses two huge detectors to analyse the results of the collisions between two high energy particle beams. These detectors, ATLAS and CMS, use electromagnets to capture and gather information about the particles that result from that collision. These magnets, require however an extremely large amount of energy to function and if operated at room temperature they would quickly overheat. The use of superconducting magnets (those that conduct electricity with no resistance) has proven to be the best method of avoiding overheating in the coils and reducing their size. To achieve superconduction the LHC magnets must be maintained at 1.9 K (-271.3°C) by a closed liquid-helium circuit. The magnets consist of conductor winding that is sealed with a resin to insulate the cable and provide strength and stiffness to the coil [106]. The selection of the resin to be used posed significant challenges as it must suit several different requirements. Hacker and Ihlein [107] listed a series of requirements for resins to be used in this application. According to their research, such resin has to exhibit sufficiently low viscosity (20 to 100 mPa.s) over the long manufacturing times required to allow the impregnation of the magnet windings, low curing temperatures (lower than 130ºC) to avoid damaging the superconducting alloys of cables, exhibit reduced shrinkage during polymerization, reduced thermal contraction between room temperature and operating temperature. It must also have good mechanical properties to be able to provide adequate mechanical strength at room temperature and a good degree of toughness and flexibility at room temperature. It must also exhibit good adhesion to the materials used in the construction of the magnet, usually non-ferrous metals and stainless steels. Evans et al [108] undertook in 1972 one of the first studies in materials for this application. A large amount of epoxy resins was tested, combined with different hardeners and fillers. Specimens were immersed in liquid nitrogen and tested, leading to the conclusion that fibre reinforcements would optimal for increased thermal shock resistance. Brennan et al [109] studied the possibility of using amine-curing systems but instead found that their developmental epoxy resins were superior in combining low viscosity with thermal shock resistance. Lastly, Rey et al [106] performed an in depth study with the aim of selecting a resin for the CERN superconductor magnets. They performed glass transition tests, measured linear shrinkage due to polymerization, determined the solid density, registered the thermal contraction from room temperature to 4 K (-269.15 ºC) and finally measured the ultimate shear strength of adhesive joint specimens at room temperature and at 4 K. They identified a formulation of resin that provided mechanical properties as good as those found in resins previously used for this purpose but with the added advantage of requiring only a temperature of 40ºC to fully impregnate the coils. Other comparable systems required temperatures above 70ºC. As an additional conclusion, they also identified that there is a lack of an adequate criterion to predict the mechanical properties of the joint at extremely low temperature, a difficulty that remains at the time of writing this document. More recently, another type of magnetic coils has been researched specifically for use in magnetic levitation high speed railways (Maglev). Electromagnets for this purpose are coated with yttrium barium copper oxide (YBCO) and are able to work at high temperature, not requiring the expensive and complex liquid nitrogen cooling systems. However, the high temperature creates problems with the epoxy coatings used for cryogenic coils and leads to premature delamination due to thermal stress [110]. The thermal stresses can break the adhesive layers and lead to separation of the coils. This is shown in Figure 9.

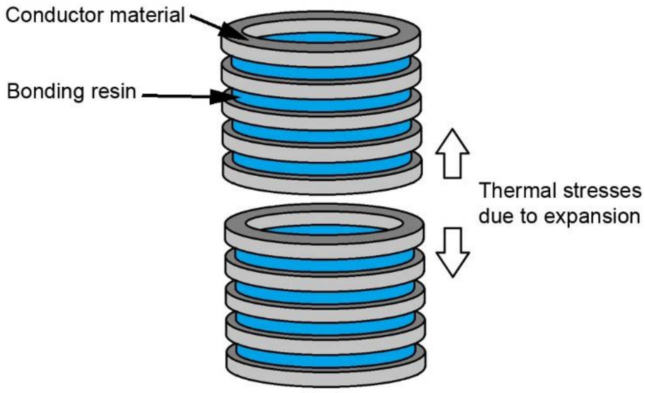

Figure 9 *- Coil construction and failure process*

Mizuno et al [111] proposed an alternate solution to bond the coils. They suggested the use of a cyanoacrylate resin and found that while the bonding strength is considerable weaker than that of epoxy resins, it is able to be used with the higher temperatures sustained by the YBCO connector without causing delamination failure.

8 Summary and future trends

The topics discussed in the course of this paper were the subject of substantial attention, devoted by researchers during the last 50 years. As a result, various practical conclusions can be extracted from the published works and directly applied on the design process of a durable and strong adhesive joint intended to be used in an extreme temperature environment.

In the topic of shrinkage, it can be concluded that shrinkage generally does not pose a problem for the failure strength of adhesive joints, generating relatively small stresses. However, the strains generated during adhesive cure can be sufficient to induce shape distortions that might be undesirable in some finished products.

The presence of thermal stresses generated by differential thermal expansion of multi-material structures is considerably more challenging. Stiff adhesives bonding metal or composite substrates will have high levels of thermal stresses and that might lead to early joint failure. But in cases where adhesives are cured and operate always above their T_g there is no generation and accumulation of thermal stresses. Adhesives, substrates and joint geometry therefore must be carefully selected to minimize these effects and avoid premature joint failure.

There have been consistent improvements in the formulations of adhesives that have greatly expanded their temperature ranges but due to their polymeric nature there are still strong performance limitations, especially when compared with mechanical fastening methods. However, as the properties of the adhesives are not the only contributing factor for joint strength and behaviour, a large amount of work is performed in improving the joint geometry. Dual adhesive joints and graded joints are valuable concepts that were recently experimentally proven and still the focus of intense research. All these advances in material properties, joint design and simulation methods, combined with a detailed knowledge of the potential problems, provide the designer of an adhesive joint with the tools to do it in a safe and efficient manner, with the full understanding of the joint behaviour under extreme thermal loads.

Acknowledgments

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Properties of RTV silicone adhesive at low temperatures

Effect of Low Temperature on Tensile Strength and Mode I Fracture Energy of a Room Temperature Vulcanizing Silicone Adhesive

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Abstract

Aerospace applications have an increasing demand for strong and reliable adhesives, able to withstand large temperature gradients. The variation of the adhesive's mechanical properties with temperature is therefore one of the factors that must be well understood before safe and reliable adhesive joints can be designed for these applications. The stress-strain curve and the toughness properties of an adhesive show strong dependency with temperature for most adhesives, especially near the glass transition temperature (T_g). In this work, an experimental procedure is undertaken to evaluate the effect of low temperatures on the adhesive strength and mode I fracture toughness of a room temperature vulcanizing silicone (RTV) adhesive. Firstly, the temperature at which the glass transition of the RTV occurs was obtained by means of an in-house developed measurement apparatus. Bulk specimens were manufactured and tested at temperatures above and below the T_g in order to obtain a strength envelope of the adhesive over this large temperature range. Single lap joints were also manufactured with this adhesive to assess the behaviour of the adhesive when assembled in a complete joint. For the determination of pure mode I fracture toughness, Double Cantilever Beam specimens were also tested at negative temperatures near T_g. The results showed that the failure loads of all the tests performed have strong temperature dependence and this must be taken into account during adhesive joint design using this type of adhesives.

K**eywords:** Room temperature vulcanizing silicone; High-temperature adhesives; Low-temperature adhesives; Single lap joint; Double cantilever beam; Fracture toughness.

1 Introduction

The severe and continuously evolving demands of the aerospace industry often require materials with highly developed mechanical characteristics, specifically designed to handle a substantial combination of mechanical and thermal loads. The sheer variety of available materials creates significant problems when the time comes to design and engineer them into a final, complete product. As such, the advanced joining techniques employed in aerospace structures are varied and of different capabilities, but among them adhesive bonding is one of the most thoroughly used, making use of highly developed adhesives that allow it to be introduced where previously it was thought to be impossible or at least not considered as an optimal solution.

An example of the type of bonding used in aerospace structures is the adhesion between a ceramic plate and metal substrate, with the objective of creating an effective heat shield [1] able to protect the underlying metallic structure from external heat. Even when the adhesive is located behind the insulation of a ceramic tile, this type of joint requires the use of an adhesive with the capability to resist considerable thermal loads without suffering lasting damage. In this application, the loss of the protecting ceramic tile means the complete loss of the thermal protection and the quick destruction of the metal structure [2]. However, high temperatures are not the only concern as the environmental conditions in aerospace applications mean that the joint will also be subjected to extremely low temperatures for a large amount of time. Therefore, there is only a limited selection of adhesives that might perform adequately under such conditions. Room temperature vulcanizing (RTV) silicone adhesives, such as the RTV106 that was used in the course of this work, are extremely versatile and have been employed in a variety of aerospace applications, mainly due to their ability to withstand extreme temperature gradients [3, 4]. While their mechanical properties are generally lower than those presented by most structural adhesives, they do have a good peel strength and can retain a good percentage of their mechanical properties over a wide range of temperatures, from cryogenic temperatures to nearly 300ºC [5, 6, 7, 8]. These adhesives cure by humidity absorption and their mechanical properties were shown by Geiss and Vogt [9] to be sensitive to the ageing in a humid atmosphere. Comyn et al [10] developed a formula to predict the curing progression for single lap joints bonded with silicone sealants, which was extended to RTV adhesives by the work of De Buyl [11]. The extensive application in joints under extreme temperature conditions is also due to the fact that they can effectively bond materials with large dissimilarity in coefficients of thermal expansion which represents a major difficulty for adhesive joints [12]. The flexibility of silicones allows them to accommodate the dimensional changes undertaken by the substrates without transferring them from one substrate to the other [13]. This is especially important when fragile substrates are used, such as the ceramic tiles common in these joints. The distinct properties of the RTV adhesive also make it very suitable to combine with a stiffer adhesive in a mixed adhesive joint, resulting in excellent mechanical strength in a large range of operating temperatures [2].

One of the other main defining properties for the suitability of an adhesive for high or low temperature applications is the glass transition temperature, commonly defined as T_g [14]. At temperatures below the T_g there is high modulus and strength combined with reduced ductility. Above T_g, the opposite is true and the adhesive will be flexible and though, but with little mechanical strength. Therefore, high temperature adhesives will generally benefit from a high T_g, while adhesives more suited for low temperature use will tend to have a low T_g. While a high temperature epoxy can exhibit a T_g near 150ºC, glass transition temperatures of RTV silicones are below zero degrees centigrade and therefore much more suited for bearing loads at low temperature. In this study, the objective was the determination of the mechanical properties of a RTV silicone adhesive subjected to low temperature conditions. Four different types of specimens were produced and tested to obtain the T_g, lap shear strength, tensile properties and mode I fracture energy.

2 Experimental details

2.1 Adhesive tested

A RTV silicone, Momentive RTV106 (Albany, NY, USA) was selected for this experimental procedure. This type of acetoxy silicone is extensively used in high temperature applications. This one-part adhesive is known for its high temperature resistance but exhibits very little mechanical strength when compared with most structural adhesives. The curing process of the RTV106 adhesive is based in the absorption of humidity from the air [11] and to ensure a complete cure, the water molecules must diffuse from the surface of the material to the interior. This makes the cure a slow process, especially when thick layers of adhesive are used, and 10 days are usually needed to ensure complete cure in the larger adhesive layers.

2.2 Specimen manufacture

2.2.1 Specimen for glass transition determination

As mentioned before there is a correlation between the strength of an adhesive at a given temperature and the adhesive's T_g. Therefore, the T_g of the adhesive is of special importance for this work. If a complete test procedure is to be performed to characterize the adhesive, it is important to understand where the glass transition zone is located.

The apparatus used for this purpose was an in-house designed apparatus which is based on the phenomenon that at the T_g of a polymer, there is a corresponding peak in the damping value. This apparatus is based on the device proposed by Zhang et al [15]. The experimental apparatus subjects a specimen, an aluminium beam with a portion of adhesive bonded to it, to a constant vibrational movement at the beam's resonance frequency. By varying the temperature in a chamber containing the specimen and registering the amplitude of movement of the specimen, the temperature at which the specimen displacement is lower can be identified. Maximum damping therefore occurs at this temperature, which can also be inferred as the temperature at which the T_g occurs.

Figure 1 shows the mechanism used to maintain the beam specimen at resonance frequency.

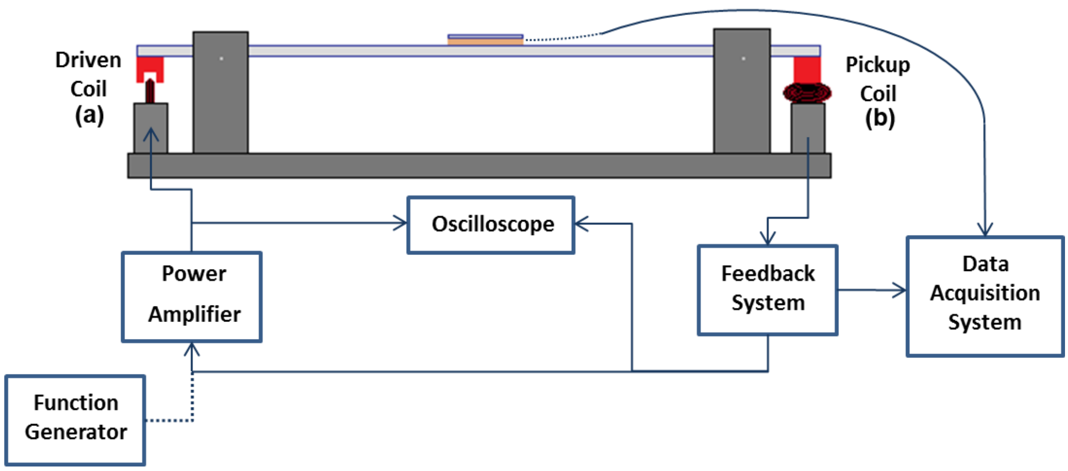

Figure 1 - Glass transition determination apparatus [16]

This system uses one driven coil (a) to excite the specimen and a pickup coil (b) to convert the beam position into an electrical signal, proportional to the amplitude of the specimen's vibration. A feedback system constantly compares the input and output signals and adjusts the input signal that is fed to the driving coil to ensure that the specimen is in resonance.

To allow the study of materials which exhibit negative T_g (such as the studied silicone) a method to adequately cool the specimen is necessary. In this work, the specimen was kept inside an expanded polystyrene insulation chamber, equipped with a liquid nitrogen injection system. By controlling the flow of liquid nitrogen fed into the chamber, the specimen temperature can be varied through a range of temperatures sufficiently low to study materials with negative T_g.

The specimens for the glass transition determination consist of a beam which has a thick layer of adhesive bonded at the middle of its span. Located on top of the adhesive layer, a small metal constraining sheet is used to amplify the effects of resonance. Aluminium of the 2024 series is used for the beams and constraining layers. Aluminium is selected for its low specific heat capacity, which ensures a homogenous temperature distribution along the specimen, and its relatively low stiffness which allows good vibration amplitude during testing and simplifies the data acquisition process. The beams have a dimension of 250x 12.5 x 3 mm^3 while the constraining sheets have 30 x 12.5 x 1 mm^3. The adhesive layer has the same width and length of the constraining layers but it has a thickness of 2 mm. Besides the specimen that vibrates, a static specimen called the dummy specimen is used only to register the temperature. These specimens are very similar in construction but have some key differences. While the dynamic specimens have ferrite magnets fastened to the extremities, the dummy specimens do not feature them but instead have a type K thermocouple embedded inside the adhesive layer.

The specimens were produced using a specially designed mould [16] which locates the beam and the constraining sheet in the correct positions while the adhesive between them cures. The mould allows the simultaneous production of the two different types of specimens. Figure 2 shows a schematic view of this mould.

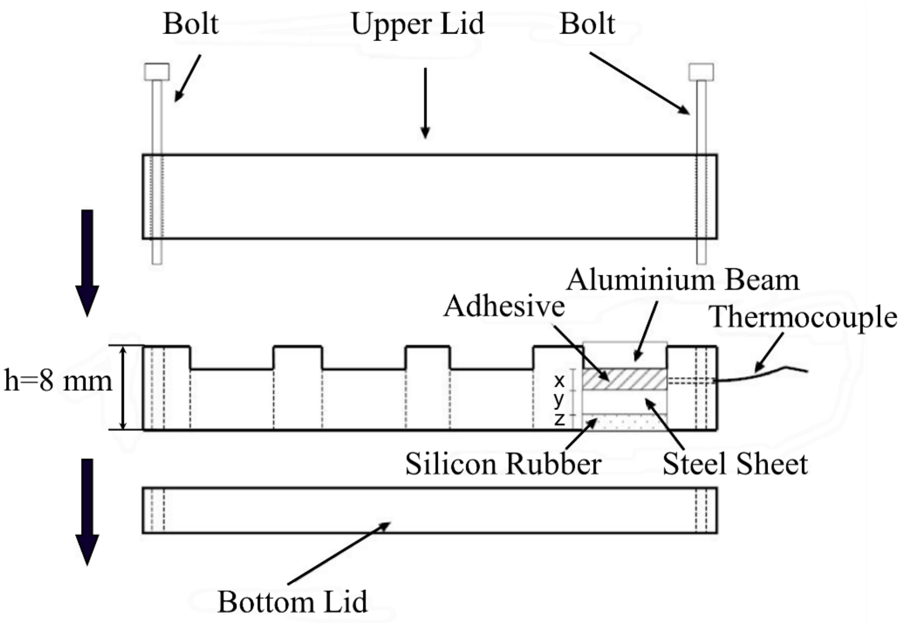

Figure 2 – Drawing of the mould for the production of T_g measurement specimens

2.2.2 Manufacture of bulk specimens

To obtain the tensile properties of the adhesive, dogbone type specimens are required. These specimens are made according to the BS 2782 standard [17] (see Figure 3) and are usually manufactured by machining a flat plate of cured adhesive to the intended shape.

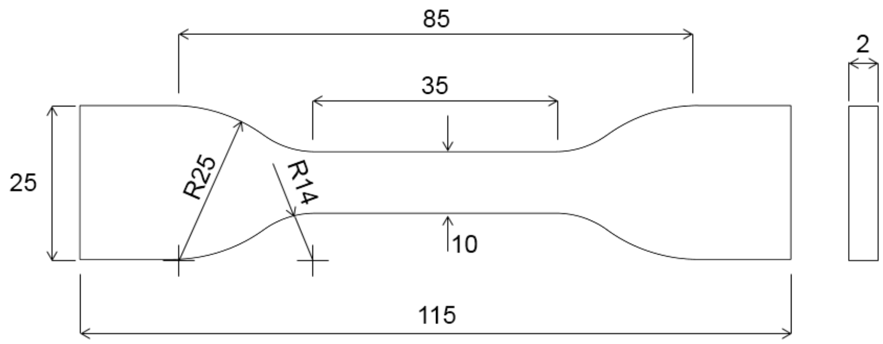

Figure 3 - Bulk specimen (dimensions in mm)

However, due to the soft consistency of the cured RTV106 adhesive, accurate machining of this material is impossible. Therefore, the specimens must be moulded directly into the final shape. The mould used for this purpose contains a laser cut stainless steel pattern, with three specimen shaped cavities. This pattern is located between two base plates with 1 mm thick silicone rubber layers separating the plates from the pattern. The whole assembly is held in place by means of four screws. When in use, all components of this mould must be covered with mould release agent, avoiding bonding between the silicone specimens and the mould [18]. Figure 4 shows this mould and the complete specimens.

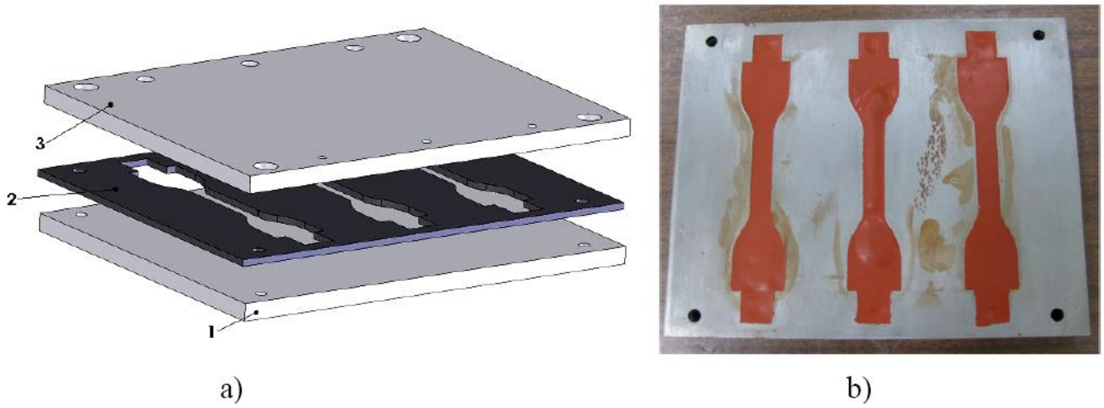

Figure 4 - a) mould for producing bulk specimens. b) cured specimens in the mould

Due to the water based curing of the silicone and the relatively large thickness and width of the specimen, the curing procedure is slow, requiring that the specimens are left 10 days in the mould at room temperature and with at least 50% of relative humidity. To reduce fluctuations, this procedure was performed in small laboratory with air conditioning. After these 10 days, the specimens can be removed from the mould but still require a further three weeks of curing exposed to ambient air. This completes the diffusion of water molecules into the material and allows the complete curing of the specimens.

2.2.3 Manufacture of single lap joint specimens

To better understand the behaviour of the adhesive when integrated in an adhesive joint complete with substrates, single lap joint specimens were produced. In these joints, aluminium alloy (6082-T651) specimens with a thickness of 3 mm and a width of 25 mm were bonded. The overlap length was 25 mm. The bondline thickness was 1 mm. The geometry of the specimens used is shown in Figure 5.

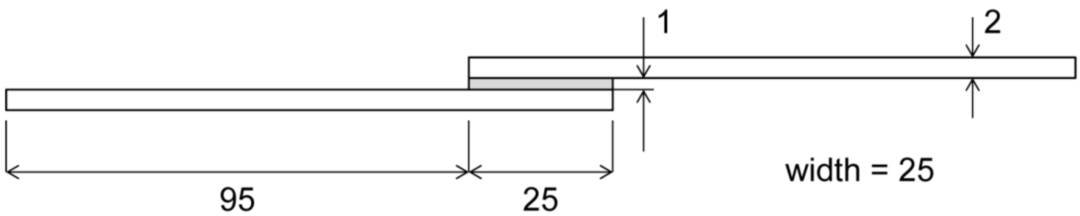

Figure 5 - Single Lap Joint specimen (dimensions in mm)

To ensure a clean bonding surface and improve the adhesion properties, the substrate surfaces were prepared by grit blasting followed by degreasing using acetone. The specimens were manufactured using a specially designed mould that ensures the correct alignment of the substrates and the inclusion of spacers. These spacers, in conjunction with the adjustment bolts, allow the control of the overlap length area but also regulate the thickness of the adhesive layer. This mould can be seen in Figure 6.

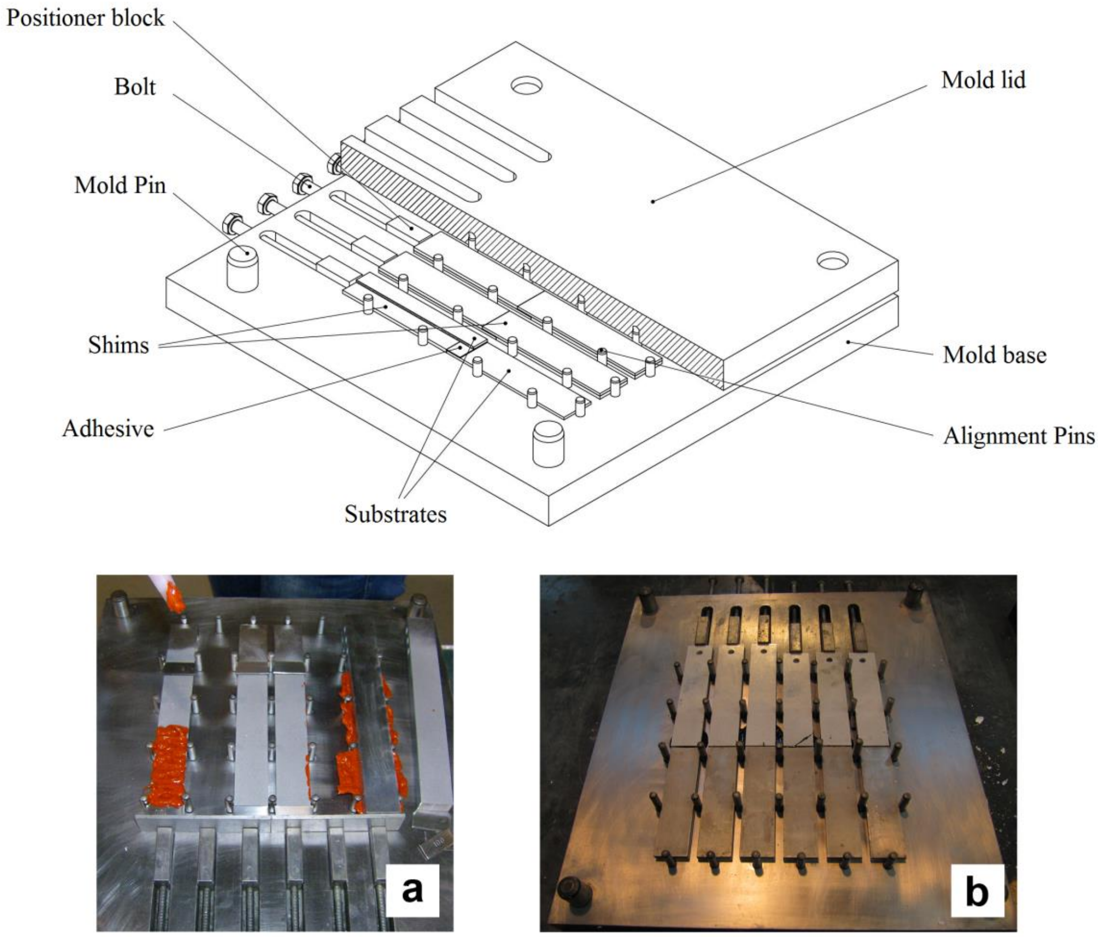

Figure 6 - Mould for manufacture of SLJ specimens. Detail a) shows the mould with DCB specimens and b) with SLJ specimens [19]

The joints were subjected to 2 MPa of pressure for 24h at room temperature. They were then removed from the press and left to cure only under the weight of the mould for an additional 7 days, following the manufacturer’s suggested curing conditions.

2.2.4 Manufacture of Double Cantilever Beam (DCB) specimens

Double Cantilever Beam (DCB) specimens were manufactured to assess the behaviour of the adhesive in a Mode I fracture loading, which is represented by a mechanical property known as the fracture toughness in mode I, abbreviated as G_{Ic}. Knowledge of fracture toughness properties is essential to allow numerical studies of adhesive joints using fracture or damage mechanics techniques.

The DCB specimen was first standardized under the ASTM D3422 standard, and now is included in the ISO 25217:2009 international standard [20, 21]. The specimen is relatively simple in construction, consisting in two beams bonded by an adhesive layer in which a crack is previously introduced. A schematic drawing of a DCB specimen can be seen in Figure 7.

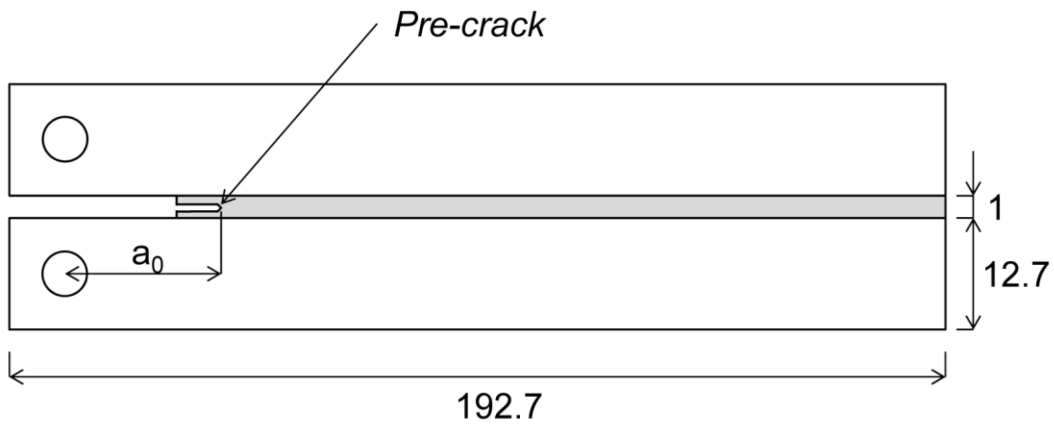

Figure 7 - Double Cantilever Beam specimen (dimensions in mm)

By exerting a force that pulls both beams apart at the section that is not bonded, the crack will advance along the adhesive layer. Stable crack propagation is the intended objective, as it allows the calculation of the fracture toughness in mode I by means of a data reduction scheme.

The DCB specimen used in this work has a steel beam with a length of 192.7 mm and a thickness of 12.7 mm while the adhesive layer is 1 mm thick. These dimensions were mainly chosen to ensure the compactness of the specimen, essential as the low temperature testing is performed in small thermal chambers [7]. The thickness is selected according to manufacturer’s recommendations, which suggest avoiding the thin layers (0.2 mm) typical of stiffer structural adhesives. As the width of the specimens is the same, the manufacturing of this specimen is done in the same mould as the single lap joint specimens, ensuring the correct alignment of the substrates [18]. The adhesive layer thickness is controlled using metallic spacers introduced between both beams. A pre-crack is generated by the use of a very thin razor blade that is placed at the tip of the adhesive layer, at exactly the mid height of the layer. The height of the blade is controlled using calibrated steel strips. The blade is bonded between the steel strips using cyanoacrylate, stacked to achieve the exact layer thickness. Each stack of blade plus calibrated steel strips is measured using a micrometer to ensure the correct thickness. The horizontal distance from the tip of this razor blade to the point where the load is applied is called a_0, and known as the initial crack length. The knowledge of this length is very important to obtain the crack propagation energy. For these tests the value of a_0 was around 65 mm, but each specimen was measured so that the a_0 value introduced in the calculations was as accurate as possible.

To evaluate the DCB test results and obtain the fracture energy during stable crack propagation in pure mode I (G_{Ic}), the Compliance-Based Beam Method (CBBM) was used. This method was developed by de Moura et al [22, 23], and is especially useful for specimens tested inside climatic chambers as it does not require an accurate measurement of the crack tip location. Instead it uses the crack equivalent concept, which is dependent only on the specimen's compliance, derived from the testing data. The equation used to obtain G_{Ic} using this method follows:

$$G_{Ic} = \frac{6P^2}{b^2 h}\left(\frac{2a_{eq}^2}{h^2 E_f} + \frac{1}{5G}\right) \tag{1}$$

where h is the specimen height, b is the specimen width, P is the applied load, G is the shear modulus of the adherends and Ef is the corrected flexural modulus. This modulus, representing the stiffness of the specimen, is obtained using a formula derived from the Castigliano theorem, with a correction needed due to the initial crack length. The formula uses the experimental data, the measured initial compliance of the DCB specimen. The formulation for the calculation of E_f can be found on Oliveira et al. [24].

The equivalent crack length, a_{eq}, is defined by:

$$a_{eq} = a + |\Delta| + \Delta a_{FPZ} \quad (2)$$

This formula takes into account the experimental compliance and the fracture process zone (FPZ) at the crack tip, where a is the real crack length, Δ is the root rotation correction for the initial crack length, obtained from the linear regression of $C^{1/3} = f(a_0)$ and Δa_{FPZ} is the correction induced by the presence of the FPZ. As with the E_f factor, the full formulation for the a_{eq} can be found in reference [24].

2.3 Test procedures

2.3.1 Bulk specimen testing

The bulk specimens were tested in a pneumatically actuated testing machine equipped with a climatically controlled testing chamber. This machine was developed in house at the Precision and Intelligence Laboratory at the Tokyo Institute of Technology. For the low temperature tests, the machine cooled the specimens to -65ºC and -100ºC using liquid nitrogen as coolant. The testing was performed at a constant rate of 1 mm/minute. The load values were obtained using the machine load cell while the strain was measured using an indirect optical method. This optical extensometer continuously measured two horizontal black marks painted on the specimen so that the deformation could be measured without the influence of the clamped section. Figure 8 shows a bulk specimen being tested at low temperature.

Figure 8 – Bulk specimen under testing at -65ºC

2.3.2 Single lap joint testing

Single lap joint testing followed a very similar procedure to the one used for the bulk specimens. The same testing machine equipped with the climatic chamber was used but with different specimen clamps to accommodate the new specimen geometry. The low temperature testing was performed at -65ºC and -100ºC and the testing rate was also a constant 1 mm/minute. The load data was obtained from the machine's load cell. As the behaviour of the full specimen is the object of the study and not only the adhesive, there was no strain measurement using the optical extensometer and the displacement was measured at the crosshead.

2.3.3 Fracture toughness testing

Fracture testing was performed using the same parameters as the single lap joint specimens and using specific clamps to hold one end of the DCB specimen. The testing speed was 1 mm/minute and the low temperature tests were only performed at -65ºC due to difficulties in gathering useful data at -100ºC. Extremely large and fluctuating loads were being measured, possibly due to ice formation between the housing and the testing clamps and no fracture energy result could be calculated with certainty from those results. The load was obtained from the machine load cell and the displacement at the crosshead was registered to be used in the calculation of the effective crack length. Figure 9 shows the setup used for testing DCB specimens.

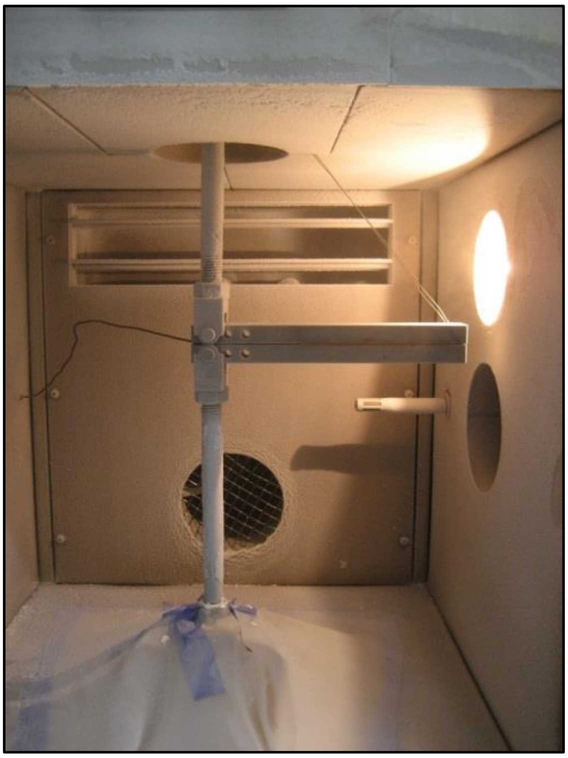

Figure 9 - Double Cantilever Beam specimen under testing -65ºC

3 Results and discussion

3.1 Glass transition temperature determination

By plotting a graph of the damping versus temperature, the T_g can be determined. Figure 10 shows a representative graph obtained for RTV106 silicone.

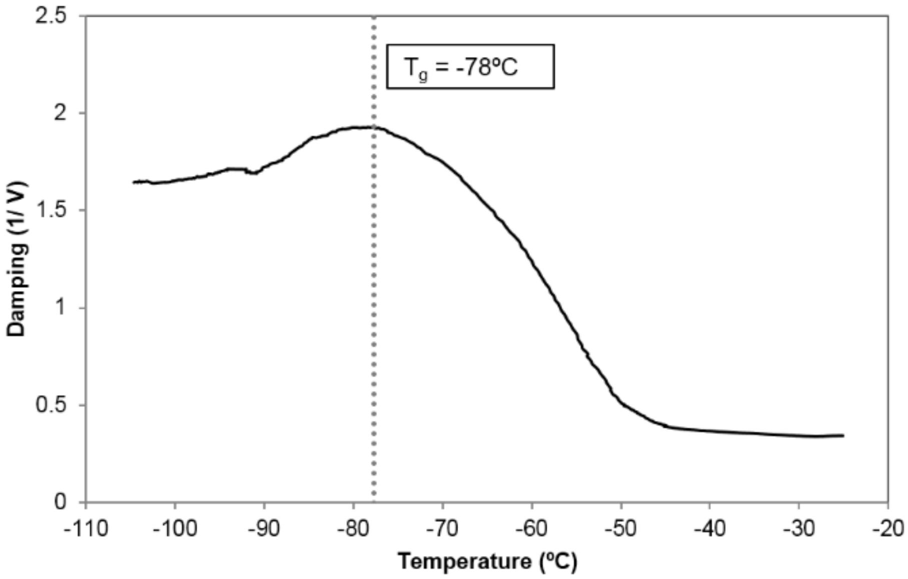

Figure 10 - Damping level variation with specimen temperature

The peak found in the damping curve corresponds to a T_g around -78ºC. The manufacturer datasheet states that the T_g of this adhesive is -65ºC. The discrepancy of 13ºC between these values cannot be considered very significant as there is a large variety of measurement methods for determining T_g and all produce changes in the specimen that translate in values that are not directly comparable. The kinetic nature of the T_g means that the heating rate and cooling rate have a significant importance in the measured result. Several comparative studies published [25-27] show that the differences can be as high as 20ºC in some cases.

3.2 Bulk specimen testing

Representative curves of bulk specimens tested at three different temperatures are shown in Figure 11. The distinct behavior of the specimens with temperature is obvious.

The specimens tested at -100ºC show large stiffness values with low deformation, while those tested at -65 and 20ºC show a large plastic phase with significant deformation.

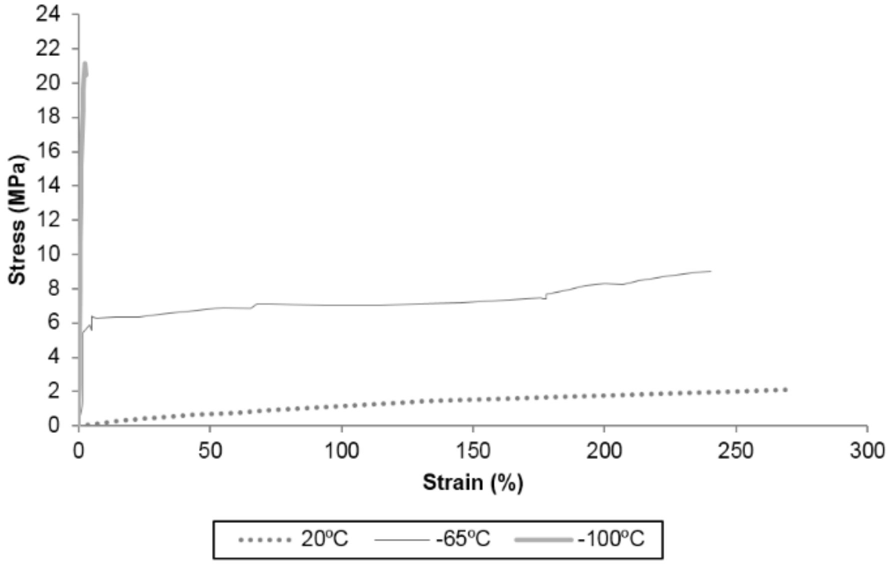

Figure 11 - Representative stress-strain curves for bulk specimens tested at three diferent temperatures

Using the data from all tested specimens, the variation of the elastic modulus with temperature can be obtained and is shown in Figure 12. The values for the Young's modulus were calculated from the tangent to the tensile stress-strain curve at the origin, with the curve represented using a polynomial approximation

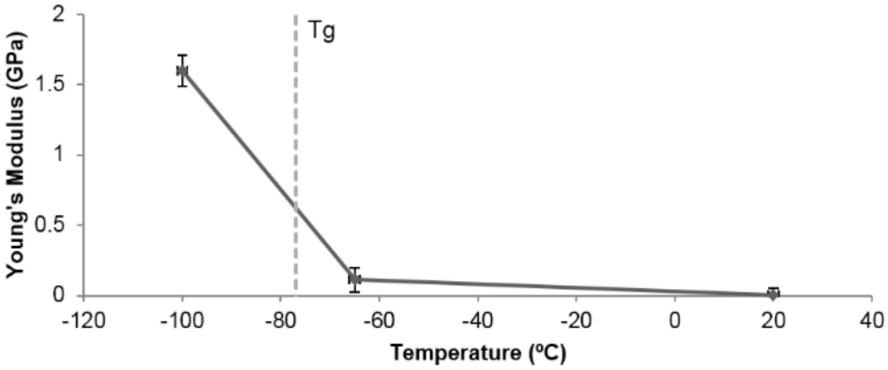

Figure 12 - Variation of the elastic modulus with temperature

The adhesive demonstrates significant temperature dependence. There is a substantial increase in elastic modulus as the temperature approaches the T_g. Passing the -65ºC data point, the adhesive becomes extremely stiff. At 100ºC, the measured modulus of elasticity is 14 times higher than the modulus registered at -65ºC. Such increase in modulus is therefore expected to translate into the failure load of the specimen. The variation of tensile strength with temperature can be seen in Figure 13.

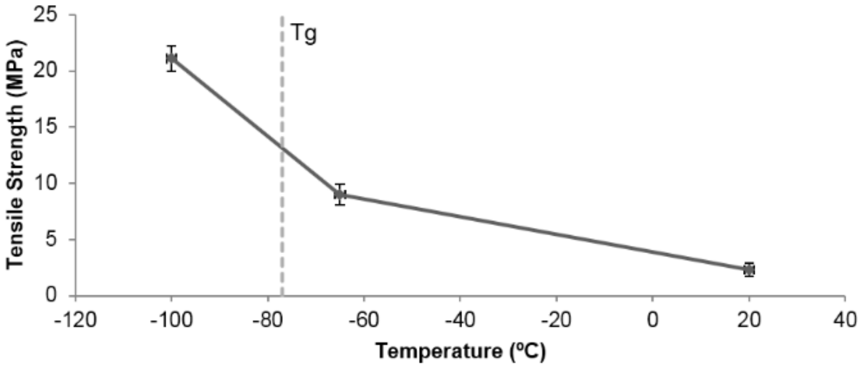

Figure 13 - Variation of ultimate tensile strength with temperature

As is the case for the elastic modulus, there is an increase in tensile strength found as the temperature reduces. However, the increase in strength does not follow the increase in tensile modulus. While the modulus is measured during the initial portion of the test, the sensitivity to micro-defects is increased in the final part of the test. This makes it very hard to achieve a comparable increase in the tensile strength of the specimen.

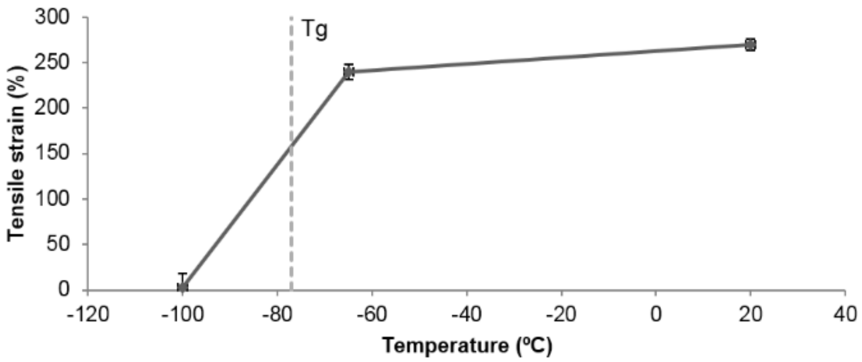

Figure 14 - Variation of tensile strain with temperature

The tensile strain variation, shown in Figure 14 follows an evolution inverse to that exhibited by the Young's modulus. At -100ºC, below T_g, the RTV adhesive has less than 3% of deformation, a value that is comparable to that of epoxies and other relatively stiff adhesives.

3.3 Single lap joint testing

The experimental results for the single lap joint test are summarized in Figure 15. This figure also includes analytical predictions for the failure load of the SLJ specimens, calculated using two different methods, as well as lap shear strength (LSS) data, calculated for each temperature.

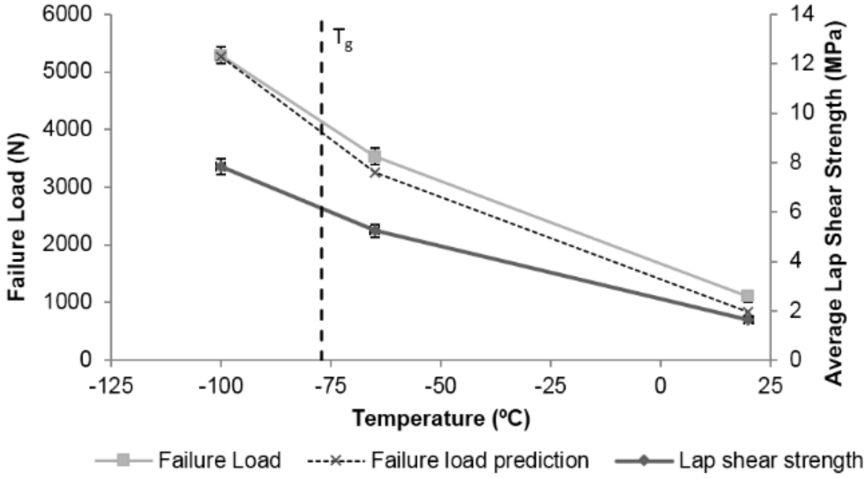

Figure 15 - Variation of SLJ failure load and average lap shear strength with temperature

The LSS for the experimental specimens is calculated by *LSS = P/bL*, where *P* is the maximum load sustained by the specimen, *b* is the joint width and *L* the overlap length. The LSS of the SLJ specimens shows a significant improvement at low temperatures, with a significant increase as the -100ºC temperature is approached. At -100ºC the LSS is approximately 470% higher than that of specimens tested at room temperature. As the temperature decreases, the displacement is also reduced. At -100ºC, the displacement is 53% less than that of the specimens tested at 20ºC. This behaviour is typical for materials approaching the T_g transition phase, where small changes in temperature result in large changes in adhesive properties.

To validate these results using data from the bulk tensile tests, failure predictions were made using two different analytical methods. These predictions are the additional data points shown in Figure 15. For the specimens tested at -100ºC, the Volkeresen's model [28] was used. In this model the failure occurs when the maximum shear stress at the ends of the overlap exceeds the shear strength of the adhesive. This model is suitable for stiff adhesives with a small plastic component. The formula used to calculate the failure load (*P*) is the following:

$$P = \tau_s \frac{2bl \sin h(\lambda l)}{\lambda l[(1 + \cos h(\lambda l)]} \tag{3}$$

Where:

$$\lambda^2 = \frac{G}{t_a}\left(\frac{2}{Et_s}\right) \tag{4}$$

and *b* is the joint width, t_a is the adhesive thickness, t_s is the adherend thickness, τ_s is the adhesive shear failure strength, *G* is the adhesive shear modulus and *E* the adherend Young's modulus. The value for τ_s is derived from the τ_n (the adhesive tensile strength obtained during bulk testing) using the following equation:

$$\tau s = \frac{\tau n}{\sqrt{3}} \tag{5}$$

The relationship between *G* and *E* is given by the following equation:

$$E = 2G(1 + \nu) \tag{6}$$

where *v* is the Poisson's ratio of the adhesive.

Table 1 lists the data used for the -100ºC Volkersen calculation.

Table 1- Data for Volkeresen calculation

	-100ºC
τ_n – tensile strength	21.1 MPa
τ_s – shear strength	12.18 MPa
b – joint width	25 mm
l – overlap length	25 mm
t_a – adhesive thickness	1 mm
t_s – substrate thickness	2 mm
$E_{substrate}$ – elastic modulus of substrate	68000 MPa
$E_{adhesive}$ – elastic modulus of adhesive	1700 MPa
$G_{adhesive}$ – shear modulus of adhesive	640 MPa

For the failure load predictions of SLJs tested at -65ºC and 20ºC, as the specimens exhibit large plasticity and deformation, the global yielding criterion [29] is more suitable. According to this model, the failure load of the adhesive is given by:

$$F_a = \tau_s b l \tag{7}$$

where F_a is the failure load of the adhesive, τ_s the shear tensile strength of the adhesive, *b* the joint width and *l* the overlap length. The value of τ_s was again related with the τ_n using Equation 5.

The data used for these two calculations is listed in Table 2:

Table 2 - Data for global yielding criterion calculation

	-65ºC	20ºC
τ_n – tensile strength	9 MPa	2.3 MPa
τ_s – shear strength	5.2 MPa	1.33 MPa
b – joint width	25 mm	
l – overlap length	25 mm	

The predictions demonstrate a good correlation between the SLJ and the bulk results, following the tendency correctly. The slight difference between the predictions and the experimental value for the SLJ specimens can in part be attributed to strain rate effects, caused by the different geometry of the specimens, leading to a higher failure load than predicted.

All specimens tested exhibited cohesive failure in the adhesive layer. Figure 16 shows a representative failure surface of a specimen tested at -65ºC.

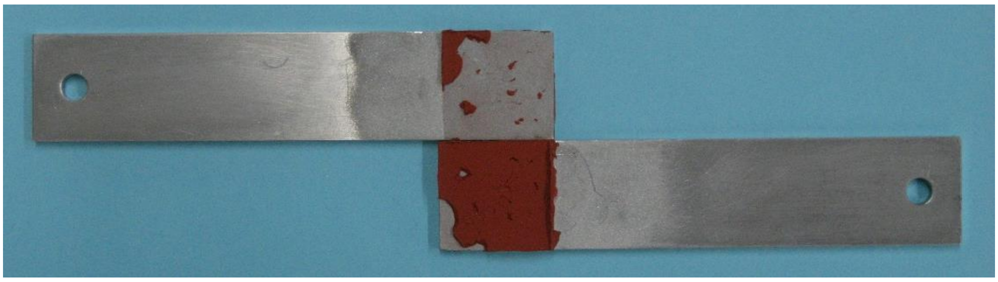

Figure 16 - Representative fracture surface of SLJ specimen (tested at -65ºC)

The SLJ results of this work were combined with previous data from Banea et al. [6]. In this work SLJ specimens with the same configuration as those presented in this work were tested at room temperature, 100ºC, 200ºC and 260ºC. The results are combined in Figure 17, illustrating the failure load and displacement at failure of SLJs as a function of temperature.

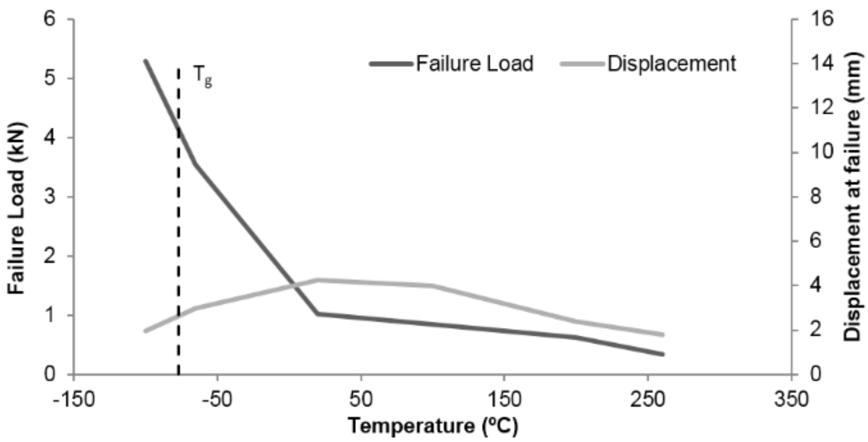

Figure 17 – Evolution of failure load and displacement at failure as a function of temperature

It can be seen that the maximum failure load is achieved close to T_g. As the temperature increases the failure load decreases because of the decrease in adhesive strength.

Close to T_g there is the best combination of strength and ductility of the adhesive. SLJ strength is dependent on both these parameters and this explains the good performance of SLJ joints at low temperature. Similar results were obtained by Banea and da Silva [30] which tested, at -40ºC, a polyurethane adhesive with a T_g of -60ºC.

3.4 Fracture toughness testing

Fracture toughness testing was performed in mode I loading, using DCB specimens. A representative load displacement curve for a DCB specimen tested at -65ºC is shown in Figure 18. A plateau with constant load can be seen. This corresponds to the stable crack propagation phase.

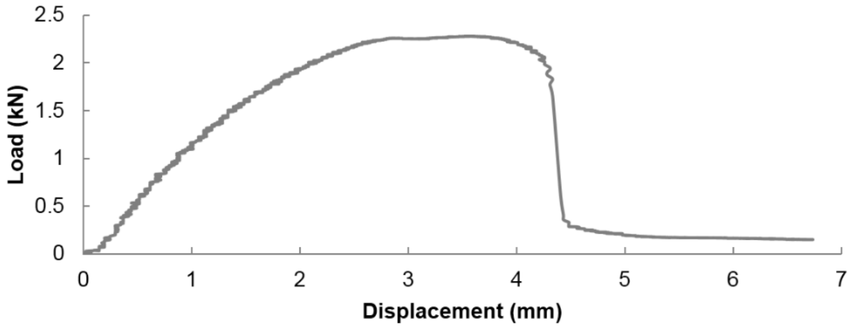

Figure 18 - Typical DCB load-displacement curve

Figure 19 shows the G_{Ic} values obtained during low temperature testing presented in conjunction with results for high temperature (100ºC and 200ºC) published by Banea et al [7]. As was found in previous tests, the mechanical properties increase close to T_g while, as the temperature increases the G_{Ic} decreases.

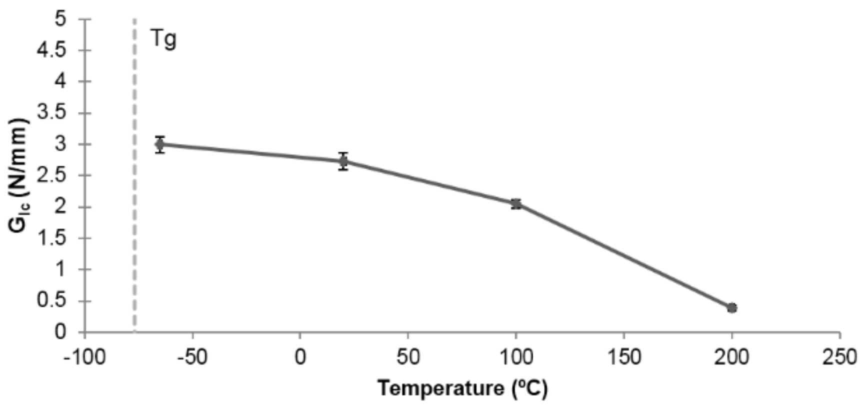

Figure 19 - Variation of G_{Ic} with temperature

G_{Ic} increased at -65ºC to a value approximately 10% percent higher than the G_{Ic} measured at room temperature. This can be explained by the fact that as the temperature decreases to -65ºC, the adhesive strength decreases and the ductility increases. As it is known, the toughness is related to strength and the ductility of an adhesive [31] and the area under the stress strain curves is related to the fracture energy. As can be observed in Figure 11, the area underneath the stress strain curve for -65ºC is clearly superior to the area under the room temperature stress strain cure leading to the increase in G_{Ic}.

All DCB specimens tested exhibited cohesive failure in the adhesive layer. Figure 20 shows a representative failure surface for a specimen tested at -65ºC.

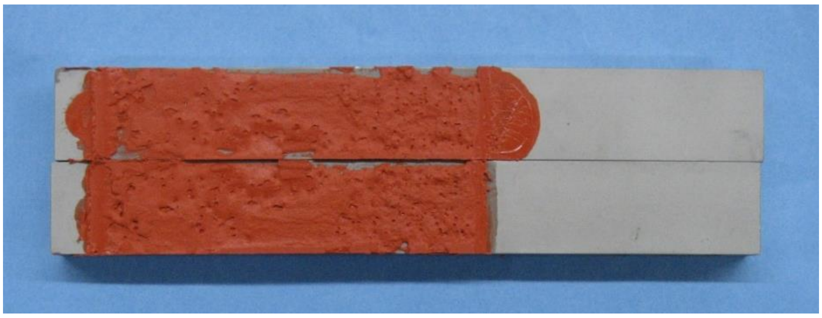

Figure 20 – Representative fracture surface of DCB specimen (tested at -65ºC)

4 Conclusions

Four different types of joints were produced and tested to determine the performance of RTV106 adhesive at various temperatures. The first test used an in-house developed apparatus to determine the T_g of the RTV106 adhesive. Using this method, the T_g was found to be around -78ºC. The bulk specimen tests, combined with Banea's previous tests [6], allowed the variation of elastic modulus to be plotted through a large temperature range. A large increase in the elastic modulus was detected between the -65ºC and -100ºC tests. This can be explained by the proximity to the temperature range where the glass transition is expected. The ultimate tensile strength for these specimens also exhibits a large increase, although it is more gradual in nature. The testing of single lap specimens demonstrated a similar tendency for the evolution of the lap shear strength. To validate the tensile properties obtained during bulk testing, these values were used to make an analytical prediction of the failure loads for the single lap joint specimens. The analytical predictions were in line with the behaviour of the experimental specimens. The DCB testing procedure was also consistent with the bulk and SLJ results, demonstrating an increase in the G_{Ic} value as the temperature decreases.

This work demonstrates that RTV silicones are very temperature sensitive and can be useful in applications which require mechanical strength in low temperature environment. With a good understanding of the thermal variation of the mechanical properties of the RTV silicones it is possible to design joints that combine them with stiffer, high temperature adhesives to obtain excellent joint behaviour in a large range of temperatures.

Acknowledgments

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Testing of ceramic metal joints at high temperatures

Experimental study of silicone-epoxy dual adhesive joints for high temperature aerospace applications

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Abstract

Adhesive bonding is extensively used in aerospace applications. Some of the most important aerospace applications are in heat shields intended to protect metallic structures from extreme heat. Many heat shields are bonded with RTV silicone based adhesives, which have excellent resistance to high temperature but very low strength. This work proposes and studies three alternate configurations to these adhesive layers. One configuration with RTV silicone only (RTV106), one with only a high temperature epoxy (XN1244) and finally another configuration introducing both adhesives in the same joint (mixed joint). Experimental specimens and a testing device intended to simulate the loads on an actual heat shield were manufactured. These specimens were subjected to loading and tested until failure at both low and high temperatures. It was demonstrated that while the RTV silicone joints lose strength at 100ºC, the epoxy and mixed joints are able to retain most of their strength. The mixed joint is also able to withstand large values of displacement at relatively high forces, indicating excellent capabilities at absorbing directed energy. The improvements and advantages deriving from the use of these alternative configurations are described and compared.

K**eywords:** Dual adhesive joints; High-temperature adhesives; RTV Silicones; Shear testing; Ceramic bonding.

1 Introduction

Adhesive bonding techniques have been extensively and successfully used in aeronautical applications during the last decades. Most of the technological breakthroughs in engineering adhesive layers have been a product of the constant progress of this industry. Structural adhesives are present in most aeronautical structures, bonding metal, polymers and composites in demanding environments that include large temperature gradients, vibrations and chemically aggressive mediums. The techniques and materials for use in aircraft are quite well developed and understood. In a more recent timescale, there has been some development in the area of high temperature bonding that allows the expansion of the usage envelope for structural bonding. These advances include adhesives exhibit the capability to withstand direct temperatures above 200ºC while providing mechanical strength sufficient to hold a structure together. This type of performance opened the door of adhesive bonding to higher performance applications, such as the bonding of high temperature heat shields in aerospace vehicles. Traditionally, this type of bonding has been performed by RTV silicones [1,2], which exhibit excellent high temperature performance but falter in various other key areas, such as shear, peel and impact resistance [3]. Heat shields for aerospace vehicles are critical and high responsibility components that must be designed as strong as technically possible to guarantee the survival of a crew and/or expensive equipment inside the vehicle. It is therefore necessary to explore the capabilities of these improved structural adhesives. This work describes a testing procedure developed to simulate a joint bonding a ceramic-metal heat shield and the typical loads associated with this type of component. Joints with a high strength/ high temperature epoxy (XN1244) [4] and a RTV silicone (RTV106) were manufactured and tested in a specially designed apparatus. In an attempt to explore the synergetic advantages of a combination between these two materials, mixed adhesive joints were also produced. The concept of a mixed adhesive joint is not new.

Many authors have proposed this technique for adhesive joints [5-9]. These joints work by combining adhesives with very diverse properties that act complimentarily to each other. Many mixed adhesive joints combine materials with different elasticity modulus to increase the joint strength. They work by applying a strong and brittle adhesive to the centre of the joint (where the displacements are reduced) and a ductile but weaker adhesive to the more mobile edges of the joint. The technique used to combine the adhesives presented in this work derives from previous work performed by the authors [10]. This creates reduced stress concentrations and smoother load distributions. These types of joints are an interesting proposition for the high temperature conditions considered in this work, an approach that was studied in detail by da Silva and Adams [11, 12]. Many adhesives intended to be used at high temperatures have very distinct mechanical properties and this situation is exacerbated by changes in these properties as the temperature increases. The study of their behaviour, alone or mixed, can provide a mechanism able to improve the mechanical resistance of ceramic metal connections.

2 Experimental details

2.1 Materials

Two distinct high temperature adhesives were chosen for the joints studied in this work. A room temperature vulcanizing silicone, Momentive RTV106 (Albany, New York, USA) was selected to perform the ductile adhesive role. This type of acetoxy silicone has been extensively used in similar high temperature applications and therefore used as an effective benchmark to test the effectiveness of the proposed joint designs. This one-part adhesive is known for its high temperature resistance but exhibits very little mechanical strength when compared with most structural adhesives. RTV106 cures in the presence of moisture and, at the thicknesses used in the experimental work described here, it requires seven days to achieve complete cure. Strength of single lap joint specimens manufactured with RTV106 are illustrated in Figure 1.This plot demonstrates the variation of strength that this adhesive suffers at high temperatures and proves its usefulness in this application.

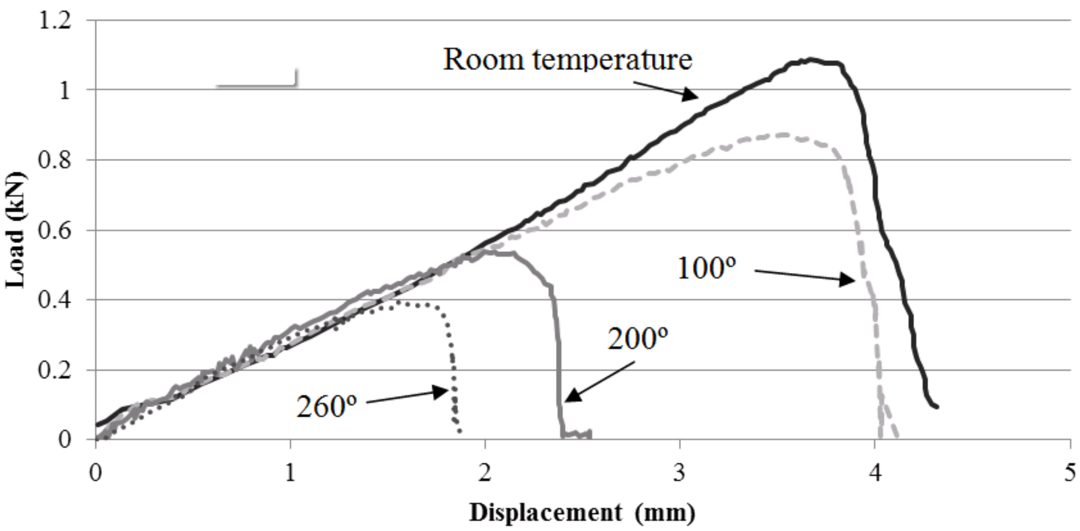

Figure 1 – Representative load displacement curves for single lap joint specimens of RTV106 at various temperatures

For the role of a stiffer, stronger adhesive, the epoxy based XN1244 produced by Nagase Chemtex (Osaka, Japan) was selected. This adhesive has excellent mechanical properties and temperature endurance. It also has good adhesion to metallic and ceramic surfaces. It is a one-part adhesive that requires a temperature of 140ºC for 1 hour to achieve full cure. This adhesive is relatively recent and as such was chosen for this work to explore its potential in high temperature aerospace usage. Figure 2 depicts stress strain curves of XN1244 bulk test specimens at high temperatures. This indicates good performance in this type of conditions.

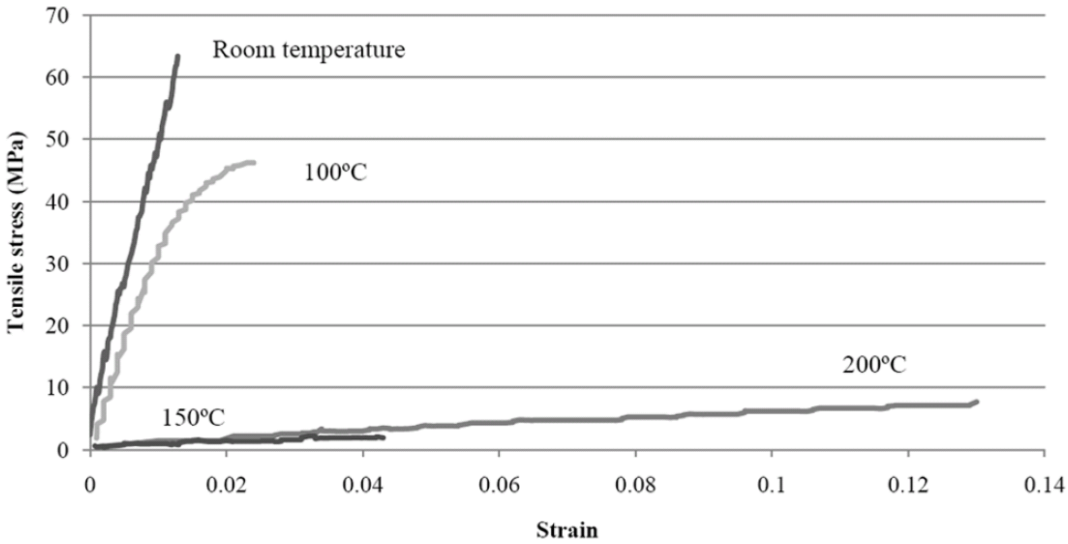

Figure 2 - Representative stress-strain curves of tensile test specimens of XN1244 at various temperatures

Cordierite is a magnesium-aluminium silicate which possesses an extremely low thermal expansion coefficient and low thermal conductivity. It is also known to resist thermal shock very effectively. This makes it a suitable candidate for the role of heat shield. The combination of these excellent thermal properties with low cost and simplicity of manufacture was the reasoning behind the use of cordierite as the heat shield material for the specimens produced during the course of this work.

For the role of the metallic substrate, aluminium 6063 T6 was used. This is a medium strength alloy, used in a variety of structural applications such as tubing, railings and electrical components. It was selected because it is also commonly used in aerospace structures. In the heat-treated condition this alloy has good resistance to various mechanisms of corrosions, including stress corrosion cracking.

Some relevant mechanical properties of the substrates are condensed in a Table 1.

Table 1- Properties of tested materials

	RTV106	XN1244	Cordierite	6063 T6
Young modulus 25ºC (MPa)	1.6	5871	70000	69500
Young modulus at 100ºC (MPa)	1.6	4466	70000	-
Poisson ratio	0.5	0.3	0.25	0.33
Tg (ºC)	-60	155	-	-

2.2 Specimens

Specimens used for this test were composed of a layered structure intended to approximate the geometry of a practical heat shield. In this specimen, a ceramic tile is bonded to an aluminium base (2 mm thick). The adhesive layer is 1 mm thick and, depending of the case studied, can be comprised of RTV106 silicone, XN1244 epoxy or both. In the case of the dual adhesive joint, the epoxy adhesive is located in the middle of the joint while the more flexible RTV106 silicone is located at the edges of the adhesive layer. The aluminium base is significantly larger than the ceramic tile and has a special hole pattern that allows it to be bolted to the testing apparatus. Figure 3 demonstrates the geometry of the specimen.

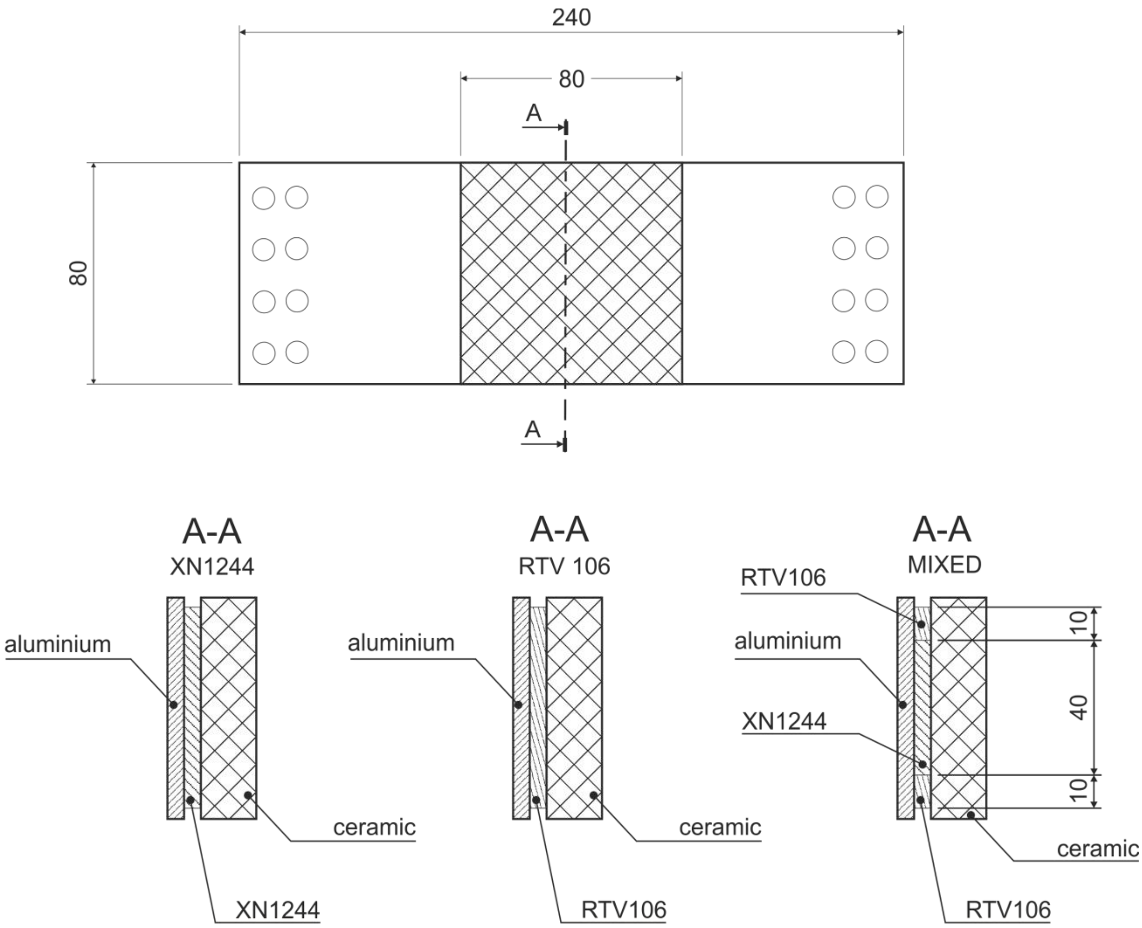

Figure 3 - Schematic view of the specimens used and the three different configurations (dimensions in mm)

The specimen is assembled in a special jig, shown in

Figure 4 that aligns all the necessary components during the stages of adhesive application and curing.

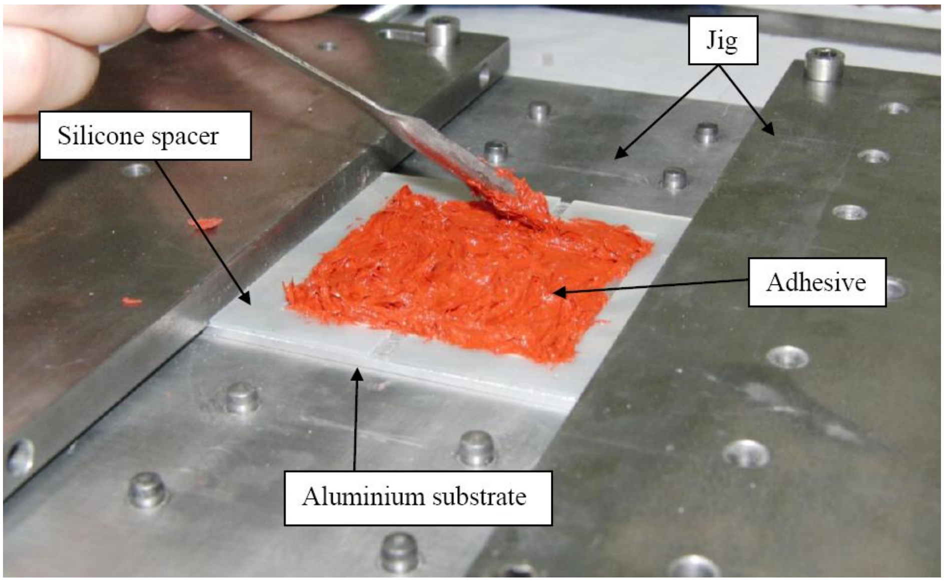

Figure 4- Adhesive application in the assembly jig

Before bonding, the substrates are prepared as follows; the aluminium substrate is sandblasted and degreased while the ceramic tile is dried at 150ºC and subsequently degreased. These steps are necessary to ensure a durable metallic ceramic bond [13]. To ensure the thickness and precise location of the adhesive layer, a 1 mm thick silicone rubber spacer is applied between the substrates. This spacer has a square, 60mm by 60 mm cut-out in the centre where the adhesive is applied. If a mixed adhesive joint is to be produced, the spacer has 3 cut-outs instead, separated by a very thin strip of silicone rubber. One is located in the centre for the stiff adhesive and two others are located in the flanks of the specimen for the flexible adhesive. These cut-outs ensure that the central epoxy section have an area of 40mm x60 mm, while the RTV sections have each 10mm x60 mm. After the adhesives are applied and the substrates bonded, the jig goes to a hot plate press for 1 hour at 140ºC (in the case of the joints with XN1244) or cures at room temperature for 24 hours (in the case of joints using only RTV106). After this initial period, the silicone rubber spacers are removed from the joint. Joints with RTV 106 must still be left curing for a further 6 days until they are ready to be tested.

2.3 Shear testing at room temperature and high temperature

This testing procedure intends to simulate the effect of a lateral force in the heat shield tile, a force such as an impact or the pressure created by very high speed airflow. The shear testing procedure was performed by mounting the specimens in a tool specially designed and built for this purpose, shown in

Figure 5.

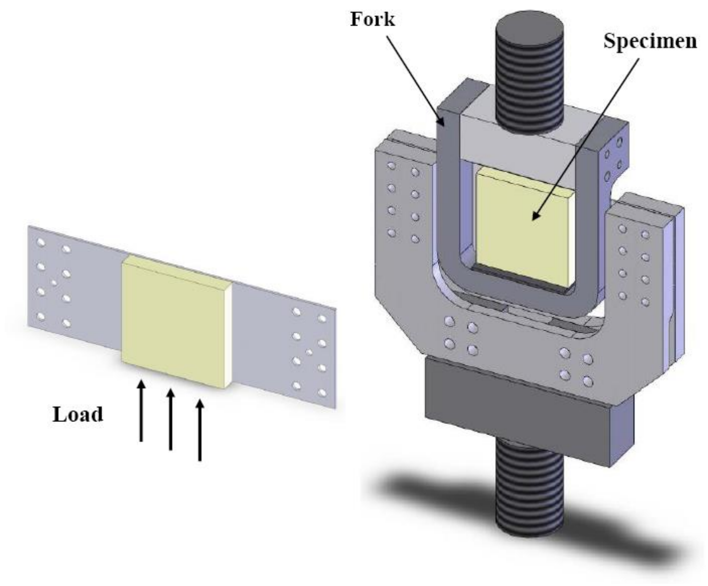

Figure 5 - Shear testing tool and specimen.

The aluminium substrate of the specimen is laid horizontally and bolted with sixteen screws to a fork-like structure that can be pulled downward by a MTS servo-hydraulic machine 321.32 (Eden Prairie, MN, USA). In the upper section of the tool, the ceramic tile is secured inside a steel frame that does not allow it to move vertically. When the bolted aluminium substrate is pulled down by the testing machine, the ceramic substrate stays in place and this introduces a large shear load component in the adhesive layer. It important to refer that a perfect shear loading is not practically achieved as the ceramic substrate still has some freedom to rotate due to the offset nature of the applied forces, the thickness of the adhesive layer and the existence of some bending in the metallic substrate. The testing tool could be easily modified to introduce a purer state of shear loading but this was decided against as it represents a departure from the actual practical application, where impacts in the ceramic can be demonstrated to produce peeling loads as well as shearing loads.

The mechanical tests were done in the MTS servo-hydraulic machine with two different speeds. 1 mm/minute was used for the RTV106 silicone adhesive and 0.5 mm/minute was used for the joints that used XN1244 epoxy (mixed or single adhesive). This speed was chosen to regulate the duration of the test based in the expected displacement and to allow a better observation of the failure mechanisms of the brittle adhesive. While it is known that the test speed can have some influence in the test results, the small difference (0.5 mm/minute) was estimated not to have any perceivable influence in the final strength of the specimens.

Shear testing was not only performed at room temperature but also at high temperature. The heating was done by a flame pointed at the ceramic surface using a pressurized gas burner to simulate the superheated air that flows over an actual heat shield. Before advancing to the actual tests at high temperature in the shear tool, an experimental setup was assembled to verify the existence of an even temperature distribution inside the adhesive layer. This step was deemed important as it ensures that internal stresses related to temperature differentials are as reduced as possible. This setup used a special specimen, instrumented with 9 thermocouples (shown in

Figure 6), a data acquisition board and a thermographic camera.

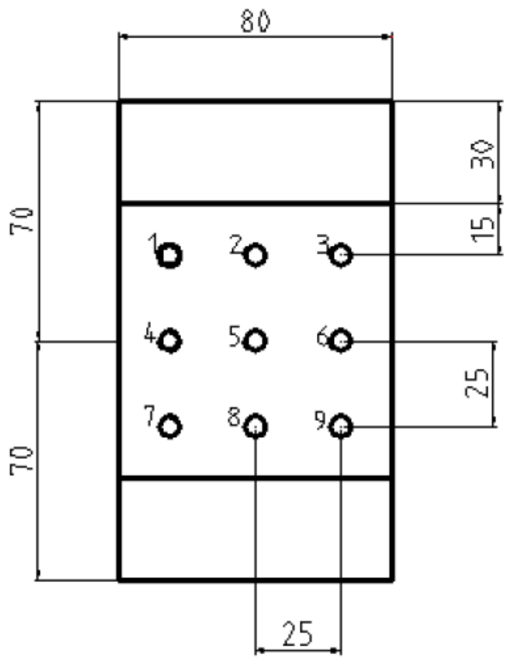

Figure 6 - Location of thermocouples in special specimen used for the study of temperature distribution

Heat was then applied to different positions of the outer surface of the ceramic tile. By continuously comparing the internal temperatures in each point of the adhesive layer, the best position to apply the flame, as well as the required gas flow, was identified. An example of temperature distribution plot is shown in Figure 7.

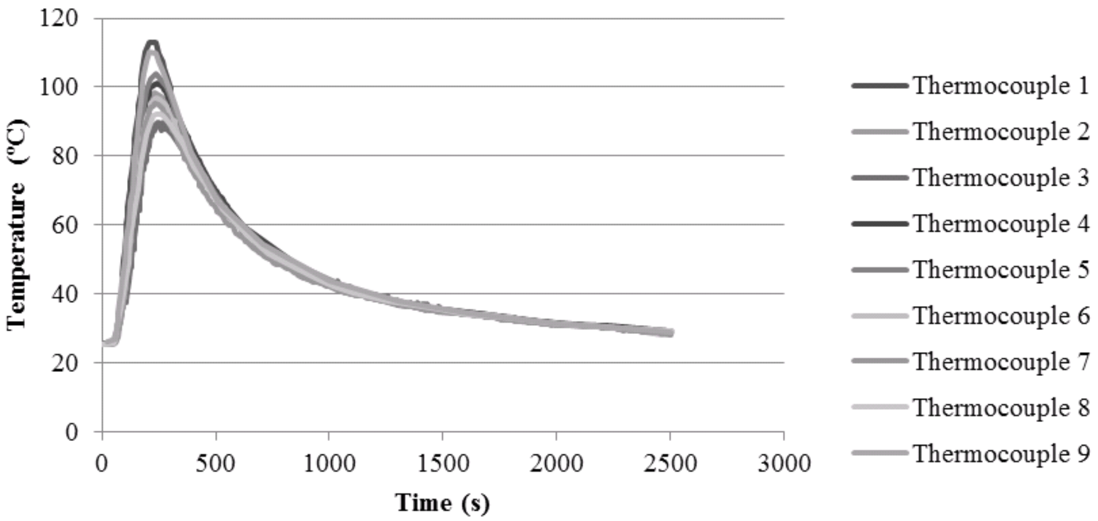

Figure 7 - Thermocouple readings during temperature distribution testing.

This graph demonstrates that during heating the thermocouples register temperature values uniformly. The biggest discrepancies are noted near the edges of the specimen where there is easier cooling. Heating power was adjusted continuously to achieve a reasonably stable temperature of 100ºC in the adhesive layer, verified with the thermocouples. This represented a surface temperature in the ceramic of around between 600 and 700º C (registered by a termographic camera in Figure 8), produced by a flame with a maximum temperature of 1750ºC (indicated by the manufacturer). These values were verified with the burner tip located 80 mm away from the ceramic tip.

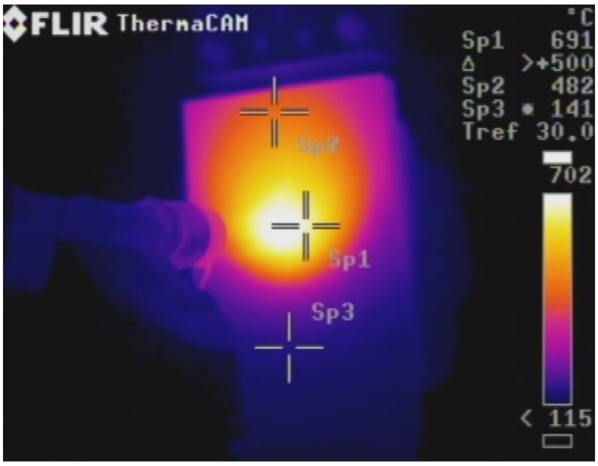

Figure 8 - Infrared image of temperatures distribution and values in the ceramic surface

This information was translated directly into the testing setup installed in the MTS servo-hydraulic machine. For simplicity reasons, each of the specimens for these high temperature shear tests only used one thermocouple to monitor the temperature inside the adhesive layer. An infrared camera was also used to monitor the temperature distribution in the back of the specimen (Figure 9).

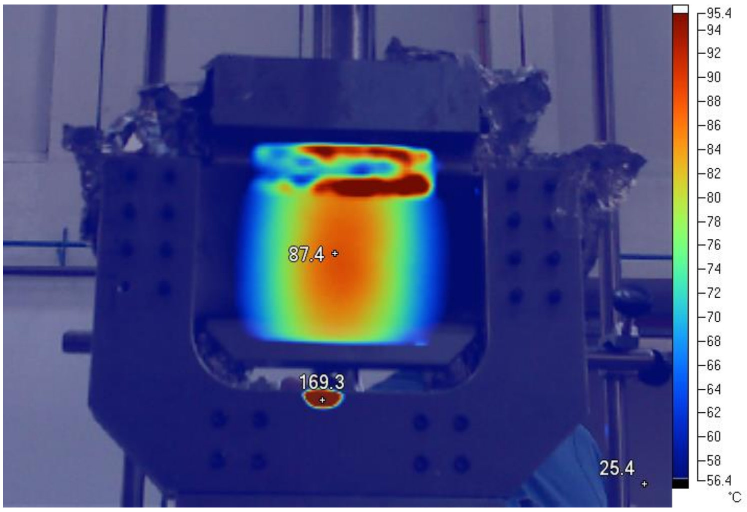

Figure 9 - Temperature distribution in the back of the metallic surface of the specimen during high temperature shear testing.

Mechanical loading was only performed when the temperature of the adhesive layer stabilized around 100ºC (+/- 5ºC). These values were controlled with a thermocouple installed in the geometric centre of the adhesive layer, at mid-thickness. Shielding was installed around the shear testing tool and the MTS hydraulic machine to ensure that the heat didn't interfere with their usage; this can be seen in Figure 10.

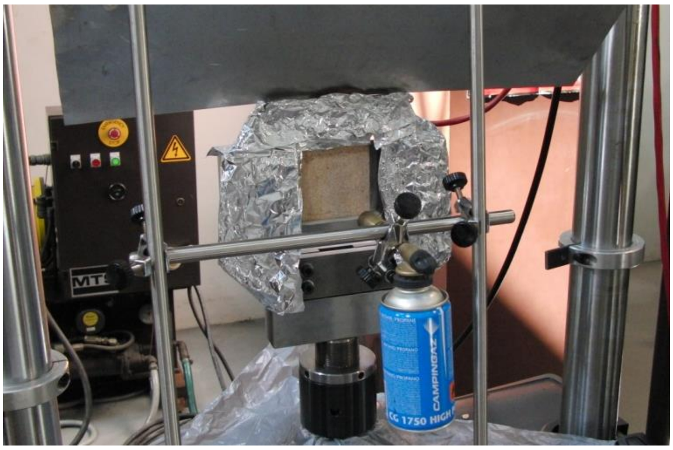

Figure 10 - Overview of final heating configuration

The number of tested specimens for each configuration and temperature is listed in Table 2.

Table 2 – Number of specimens tested for each configuration

	Room temperature	100ºC
XN 1244 joint	5	3
RTV106 joint	4	4
Mixed adhesive joint	4	4

3 Results

3.1 Shear testing

The average failure loads for the room temperature tests are presented in Figure 11.

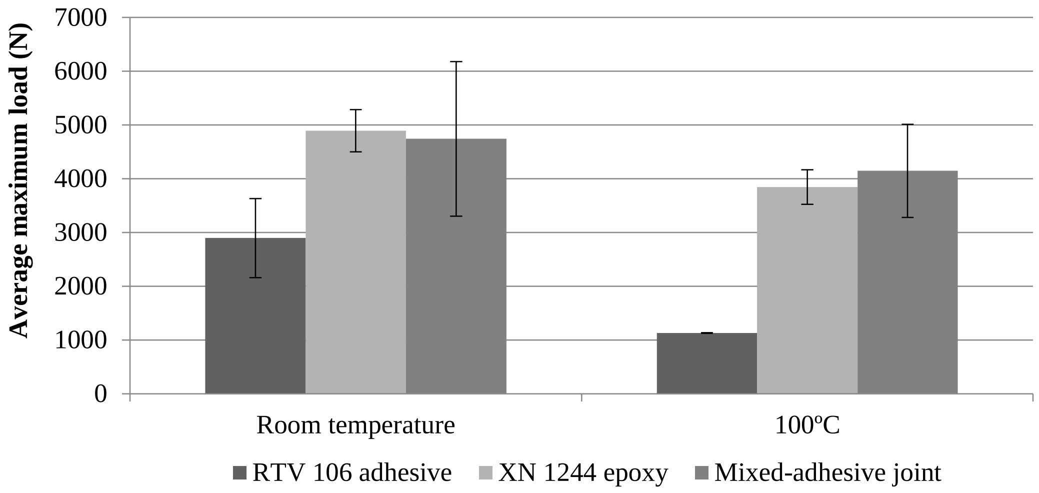

Figure 11 - Average maximum loads for shear tests of all specimens

At room temperature, XN1244 epoxy is the best performing adhesive layer, with a slight advantage over the mixed joint. RTV106 silicone joints exhibit lower strength. At higher temperatures, Figure 11 shows that RTV silicone joints lose a large percentage of strength; there is a reduction from 3 kN to slightly over 1 kN. In contrast, the mixed joint and the XN1244 joints have a less pronounced strength loss, although with an inversion of the strongest type of joint.

All of the joints failed cohesively. The joints using only RTV106 silicone had cohesive failure in the adhesive (shown in Figure 12), while the joints that used XN1244 had cohesive failure in the ceramic substrate (this can be seen in Figure 13). This means that the upper limit for the joints that used XN1244 is not necessarily the adhesive itself but the resistance of the ceramic tile.

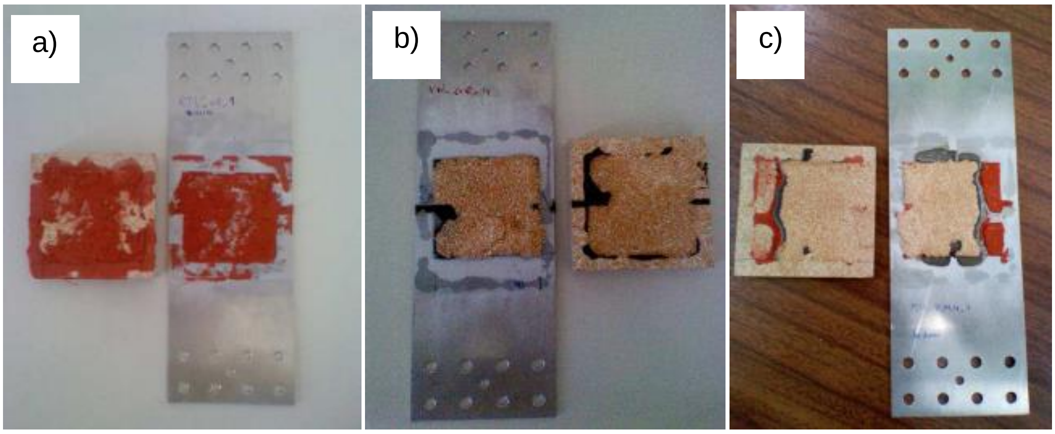

Figure 12 – Example of cohesive fracture of specimens tested at room temperature. Legend: a) RTV106 specimen, b) XN 1244 specimen, c) Mixed adhesive joint.

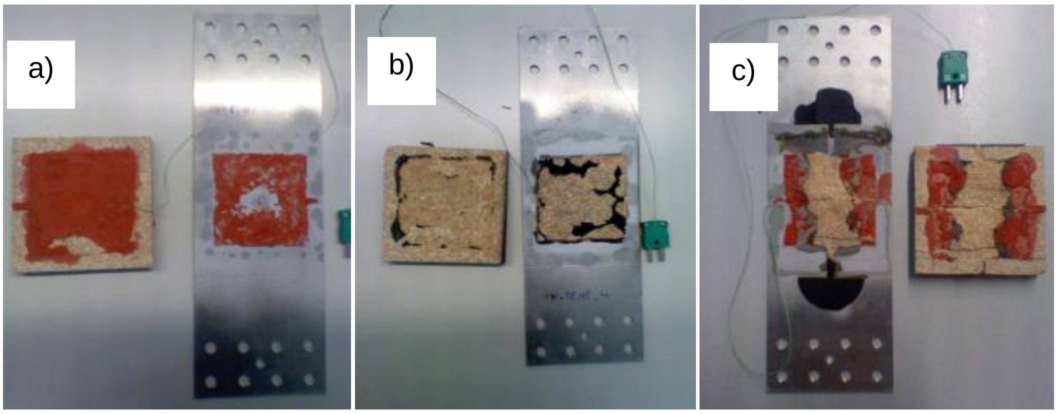

Figure 13 – Example of cohesive fracture of specimens tested at 100ºC. Legend: a) RTV106 specimen, b) XN 1244 specimen, c) Mixed adhesive joint.

The failure process of the ceramic tile is also different between joints. Joints manufactured using only XN1244 fail in a brittle and sudden manner, with the complete projection of the ceramic tile away from the specimen. The joints that use RTV106 do not allow this type of failure mode. The ceramic tile is kept in position even when the adhesive layer has been deprived of most of its strength. This type of failure is especially interesting for the intended application.

The progressive loss of strength of the mixed adhesive joints can also be inferred from the maximum displacements verified. As it can be seen in Figure 14, the presence of RTV106 silicone in the mixed adhesive joints allows it to have a significantly higher displacement than the XN1244 joints at high temperature but also with higher strength. This is caused by progressive yielding of the adhesive layer.

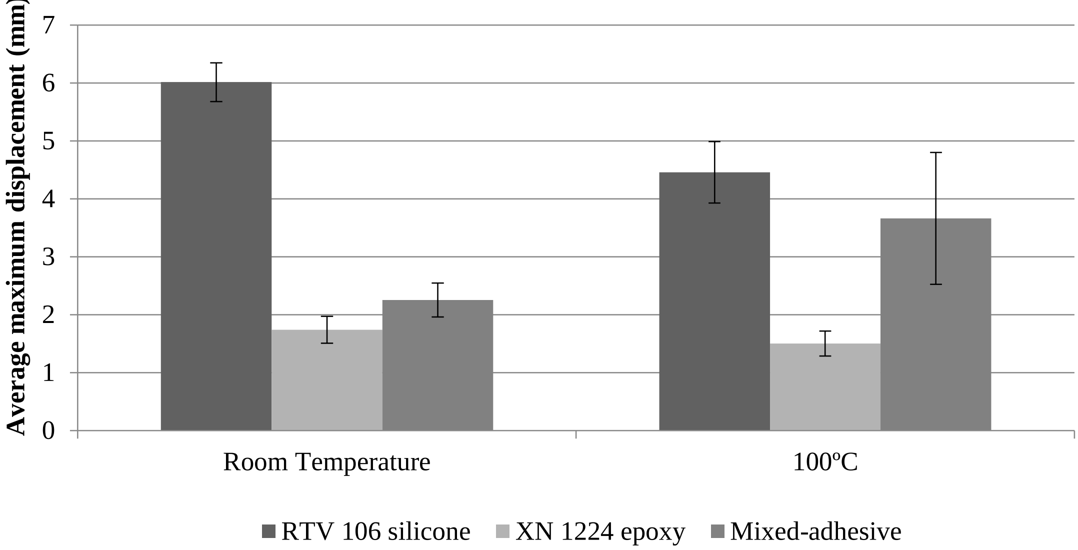

Figure 14 - Average maximum displacements for shear tests of all specimens

This can be seen in the force-displacement graphs registered during testing at high temperature, plotted in Figure 15.

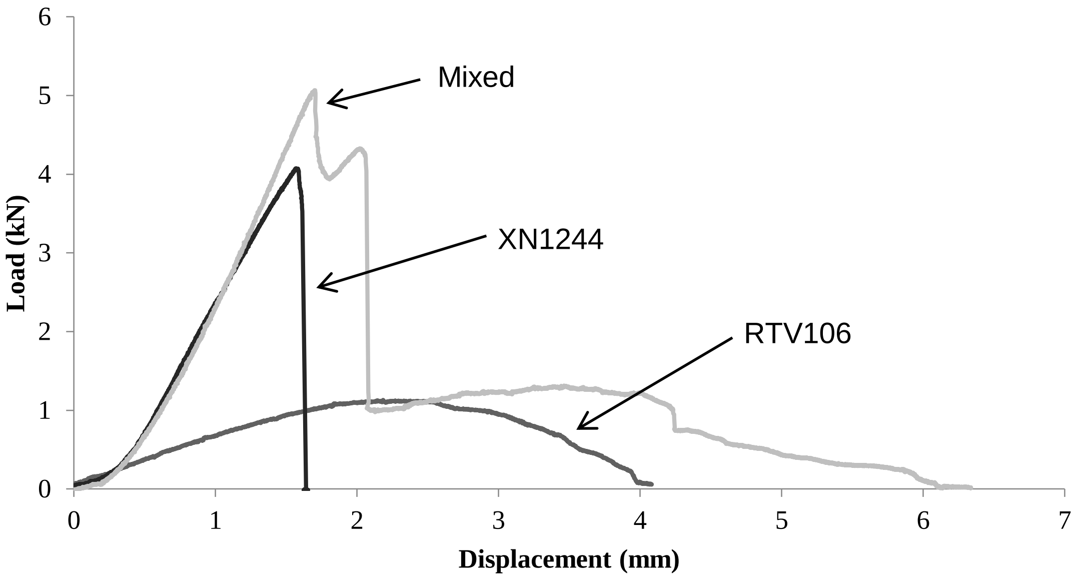

Figure 15 - Representative load-displacement curves for all specimens at 100ºC

The progressive failure and peaks represent the transition of load from the strongest and stiffest epoxy centre section to the weaker and more ductile silicone outer sections.

As different sections of the epoxy layer fail a series of successive peaks appear in the load graph. When the entire epoxy layer has been rendered incapable of carrying load, the silicone layers take over and allow the achievement of high values for maximum displacement (comparable to those of RTV silicone alone), even after the ceramic tiles breaks. This phenomenon of progressive failure is not exclusive to the high temperature tests. Though the effect is less pronounced, Figure 16 demonstrates its existence at room temperature.

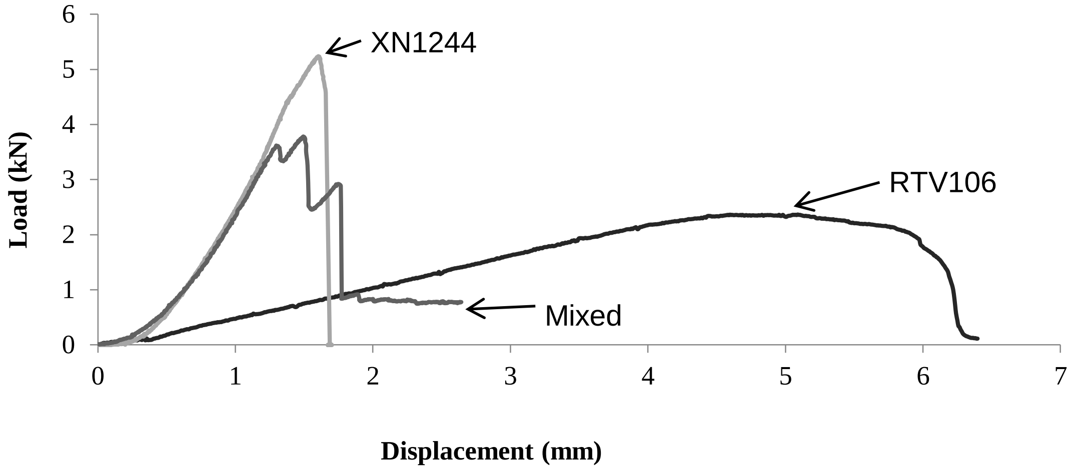

Figure 16 - Representative load-displacement curves for all specimens at room temperature

As mentioned before, this behaviour of the silicone layer improves the practicality of the joint although its mechanism of actuation leads to more dispersion in the results when compared to a single adhesive.

This phenomenon also has direct implications in the energy absorption rates of each joint. The energy absorption for each test is plotted in Figure 17.

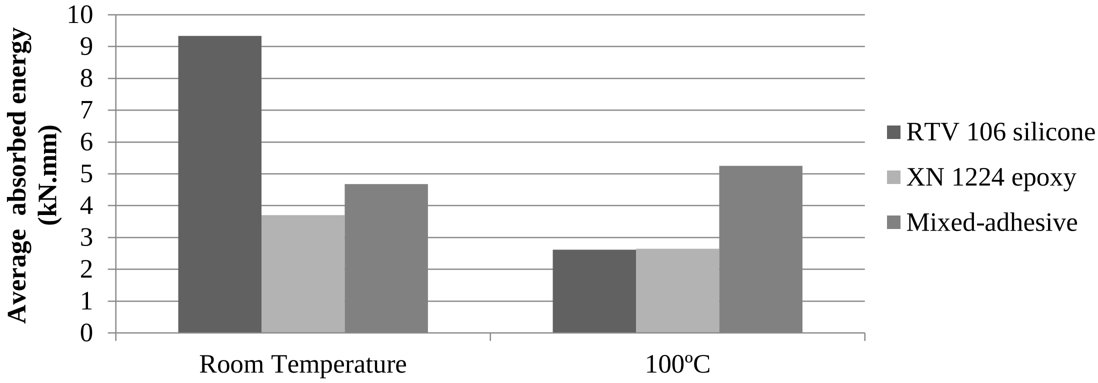

Figure 17 - Average absorbed energy for shear tests of all specimens

RTV106 silicone has the highest absorbed energy at room temperature but has a steep reduction of that value at 100ºC. The mixed adhesive joint, when at room temperature, exhibits similar energy absorption as the XN1244 joint but at the higher temperature manages to keep the energy absorption value relatively higher. This indicates a stronger capability to withstand impact forces in high temperature conditions.

4 Conclusions

The behaviour of a joint representative of an aerospace heat-shield was studied and tested with a device intended to produce failure under a shearing load at room temperature and at high temperatures. Two different adhesives and a further additional combination of the two were used in the adhesive joint.

The highest overall loads are achieved by use of the XN1244 epoxy at room temperature. This adhesive has much improved mechanical performance over the RTV106 silicone, with similar insensitivity at high temperatures.

The XN1244 epoxy joints and mixed adhesive joints were found to be limited not by the strength of the adhesive layer but by the strength of the ceramic. If we take into account the fact that RTV silicone is used standalone in various applications, we can conclude that these XN1244 joints exhibit sufficiently improved shear strength over the RTV joints. The brittle nature of the XN1244 epoxy joints can be corrected with the addition of RTV106 joints, resulting in a stronger and safer joint.

Mixed adhesive joints kept their strength at 100ºC while the RTV silicone joints exhibited a large drop of strength. They also achieved this strength with much more displacement than the XN1244 joints. Joints containing RTV106 silicone do not release the ceramic tile during tests. This means that even if the adhesive layer is damaged, the ceramic tile might still be able to shield the structure effectively.

Acknowledgments

FCT (Fundação da Ciência e Tecnologia) is thanked for financing the project (PTDC/EME-PME/67022/2006 – P0716) in which this work is included.

Nagase-Chemtex is also gratefully acknowledged for supplying free adhesive samples.

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Testing of ceramic-metal joints at low temperatures and under impact

Testing of dual adhesive ceramic-metal joints for aerospace application

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Abstract

Aerospace structures are often complex combinations of high performance materials, carefully optimized to withstand extreme working conditions. Aerodynamic forces, wide temperature range, vacuum and impacts are powerful forces that require these structures to be designed using only the strongest materials and most reliable construction techniques. Among these structures are heat shields for aerospace applications, components comprised of various layers, intended to protect the metallic structures of a vehicle from high temperatures. This work proposes and studies three alternate configurations to these layers, using adhesives to bond the shield together. One configuration with RTV silicone only (RTV106), one with only a high temperature epoxy (XN1244) and finally another configuration introducing both adhesives in the same joint (mixed joint). Experimental specimens and a testing device intended to simulate the loads on an actual heat shield were fabricated. These specimens were subjected to loading and tested until failure at three different temperature levels (-65ºC, 25ºC, 100ºC). Impact testing was also performed to assess the suitability of each configuration to withstand direct impacts.

Keywords: Dual adhesive joints; High-temperature adhesives; Low-temperature adhesives; RTV Silicones; Shear testing; Ceramic bonding; Impact testing.

1 Introduction

Adhesive bonding techniques have been extensively and successfully used in aeronautical applications during the last decades. Most of the technological breakthroughs in engineering adhesive layers have been a result of the continued progress of this industry. Structural adhesives are present in most aeronautical structures, bonding metals, polymers and composites in demanding environments that include large temperature gradients, vibrations and chemically aggressive media [1]. The techniques and materials for use in aircraft are quite well developed and understood. More recently, there has been some development in the area of high temperature bonding that allows the expansion of the usage envelope for structural bonding. These advances include adhesives exhibiting the capability to withstand direct temperatures above 200ºC while providing mechanical strength sufficient to hold the structure together. This type of performance opened the door for adhesive bonding to be used in high performance applications, such as the bonding of high temperature heat shields in aerospace vehicles. Traditionally, this type of bonding has been performed by RTV silicones [2,3], which have a consistent mechanical behaviour in a large range of temperatures but are known to have little overall strength, which can be detrimental in impacts or collisions where there is a large force acting directly on the adhesive layer. [4,5]. Heat shields for aerospace vehicles are critical and high responsibility components that must be designed as strong as technically possible to guarantee the survival of the crew and/or expensive equipment inside the vehicle. It is, therefore, necessary to explore the capabilities of these improved structural adhesives. This work describes a test procedure developed to simulate a joint bonding a ceramic-metal heat shield and the typical loads associated with this type of component. Joints with a high strength/ high temperature epoxy (XN1244) [6-8] and a RTV silicone (RTV106) were fabricated and tested in a specially designed apparatus proposed in a previous paper by the authors [9]. In an attempt to explore the synergetic advantages of a combination of these two materials, mixed adhesive joints were also produced. The concept of a mixed adhesive joint is not new. Many authors have proposed this technique for adhesive joints [10-14]. These joints work by combining adhesives with very diverse properties that act complimentarily to each other. Many mixed adhesive joints combine materials with different elasticity moduli to increase the joint strength. They work by applying a strong and brittle adhesive to the centre of the joint (where the displacements are reduced) and a ductile but weaker adhesive to the more mobile edges of the joint. The technique used to combine the adhesives presented in this work derives from previous work performed by the authors [15]. This creates reduced stress concentrations and smoother load distributions. These types of joints are an interesting proposition for the high temperature conditions considered in this work, an approach that was studied in detail by da Silva and Adams [16, 17]. Many adhesives intended to be used at high temperatures have very distinct mechanical properties and this situation is exacerbated by changes in these properties as the temperature increases. The study of their behaviour, alone or mixed, can provide a mechanism able to improve the mechanical resistance of ceramic-metal connections.

The test procedures to which these joints were subjected was developed to be a good representation of the demanding requirements during the service life of a joint intended to be used for aerospace applications. It includes static testing in a large range of temperatures and impact testing. The tests presented here are a follow-up to the testing program previously presented for this specimen configuration [9] but with the significant addition of low temperature and impact testing.

Analysis under impact is extremely relevant for this application. In a bonded heat shield assembly, the worst case scenario is a high speed collision of debris against the ceramic tile. Despite the low mass of the particles that can hit the ceramic tile, the velocities involved are usually very high, causing substantial damage that can completely disrupt the thermal protection conferred by the ceramic tile. Under impact, adhesives are known exhibit reduced ductility, coupled with higher stress level when compared with a quasi-static test. This type of loading results in high failure loads coupled with reduced absorbed energy [18]. It is important to study and understand this difference between impact and static testing before recommending a specific adhesive configuration for the intended application and as such, impact testing is a very significant part of the test procedure hereby presented.

2 Experimental details

2.1 Materials

Two distinct high temperature adhesives were chosen for the joints studied in this work. A room temperature vulcanizing silicone, Momentive RTV106 (Albany, NY, USA) was selected to perform the ductile adhesive role. This type of acetoxy silicone has been extensively used in similar high temperature applications and, therefore, was used as an effective benchmark to test the effectiveness of the proposed joint designs. This one-part adhesive is known for its high temperature resistance but exhibits very little mechanical strength when compared with most structural adhesives. RTV106 cures in the presence of moisture and, at the thicknesses used in the experimental work described here, it requires seven days to achieve complete cure. Strength of single lap joint specimens fabricated with RTV106 is illustrated in Figure 1. This plot demonstrates the variation of strength that this adhesive suffers at high temperatures and illustrates its usefulness in this application. More testing of RTV106 single lap joint specimens can be found in Banea et al. [6].

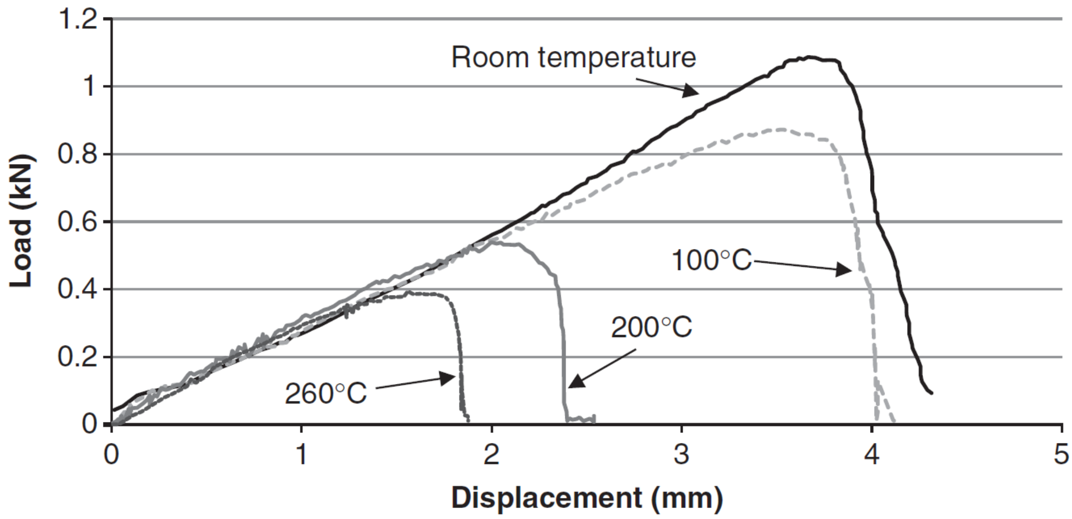

Figure 1 – Representative load-displacement curves for single lap joint specimens of RTV106 at various temperatures [6]

For the role of a stiffer, stronger adhesive, the epoxy based XN1244 produced by Nagase Chemtex (Osaka, Japan) was selected. This adhesive has excellent mechanical properties and temperature endurance. It also has good adhesion to metallic and ceramic surfaces. It is a one-part adhesive that requires a temperature of 140ºC for 1 hour to achieve full cure. This adhesive is relatively recent and as such was chosen for this work to explore its potential in high temperature aerospace usage. Figure 2 depicts stress-strain curves of XN1244 bulk test specimens at high temperatures. This indicates good performance in this type of conditions.

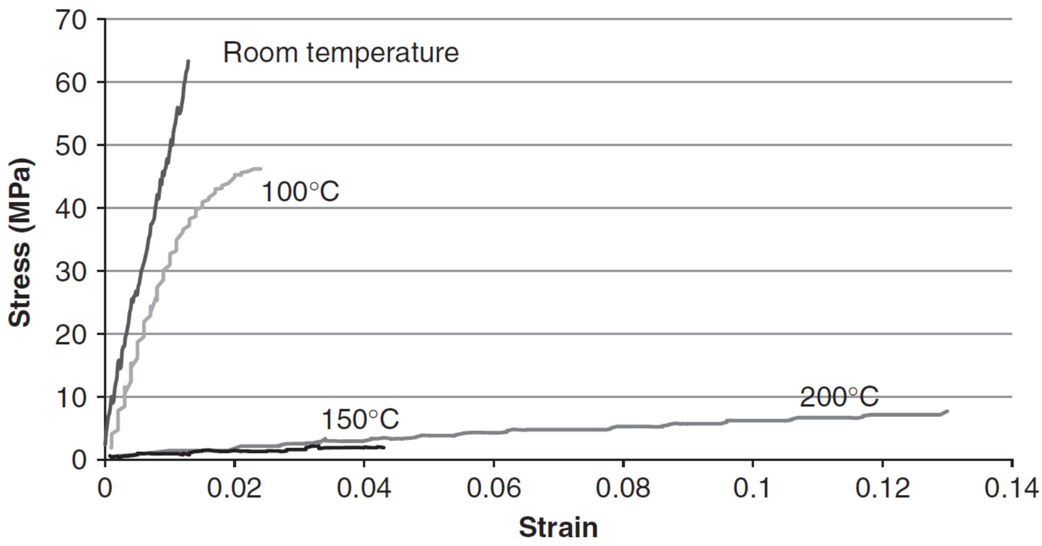

Figure 2 - Representative stress-strain curves of tensile test specimens of XN1244 at various temperatures [6]

Cordierite is a magnesium-aluminium silicate which possesses an extremely low thermal expansion coefficient and low thermal conductivity. It is also known to resist thermal shock very effectively. This makes it a suitable candidate for the role of heat shield. The combination of these thermal properties with low cost and simplicity of fabrication was the reasoning behind the use of cordierite as the heat shield material for the specimens produced during the course of this work.

For the role of the metallic substrate, 6063 T6 aluminium was used. This is a medium strength alloy, used in a variety of structural applications such as tubings, railings and electrical components. It was selected because it is also commonly used in aerospace structures. In the heat-treated condition this alloy has good resistance to various mechanisms of corrosions, including stress corrosion cracking.

Some relevant mechanical properties of the substrates are condensed in Table 1.

Table 1- Properties of tested materials

	RTV106	XN1244	Cordierite	6063 T6 aluminum
Young's modulus at 25ºC (MPa)	1.6	5871	70000	69500
Young's modulus at 100ºC (MPa)	1.6	4466	70000	677000
Poisson's ratio	0.5	0.3	0.25	0.33
Tg (ºC)	-60	155	-	-

2.2 Specimens

Specimens used for this test were produced with a layered structure intended to approximate the geometry of a practical heat shield. In this specimen, a ceramic tile was bonded to an aluminium base (2 mm thick). The adhesive layer was 1 mm thick and, depending of the case studied, could be comprised of RTV106 silicone, XN1244 epoxy or both. In the case of the dual adhesive joint, the epoxy adhesive was located in the middle of the joint while the more flexible RTV106 silicone was located at the edges of the adhesive layer. The aluminium base was significantly larger than the ceramic tile and had a special hole pattern that allowed it to be bolted to the test apparatus. Figure 3 depicts the geometry of the three configurations of the specimens tested.

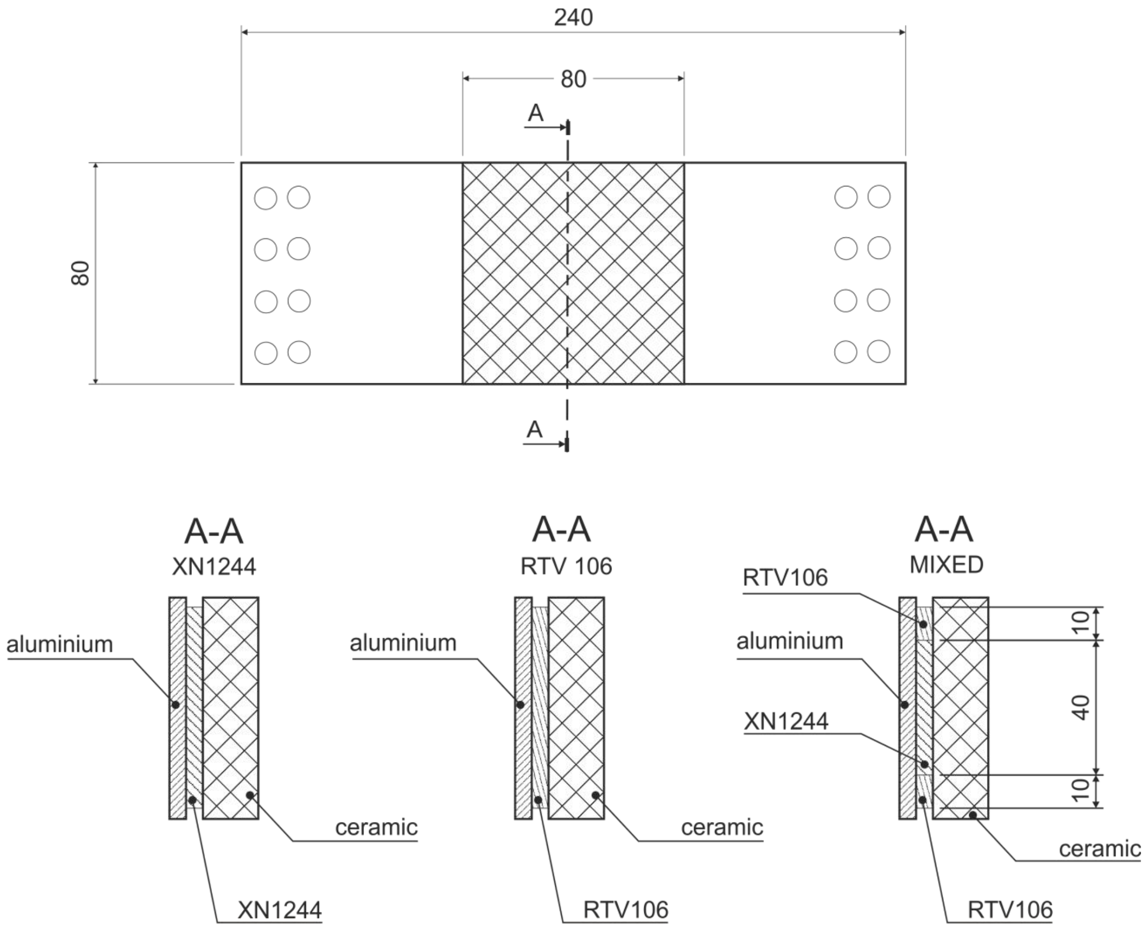

Figure 3 - Schematic views of the specimens used and the three different configurations (dimensions in mm)

The specimen was assembled in a special jig, shown in Figure 4 that aligned all the necessary components during the stages of adhesive application and curing.

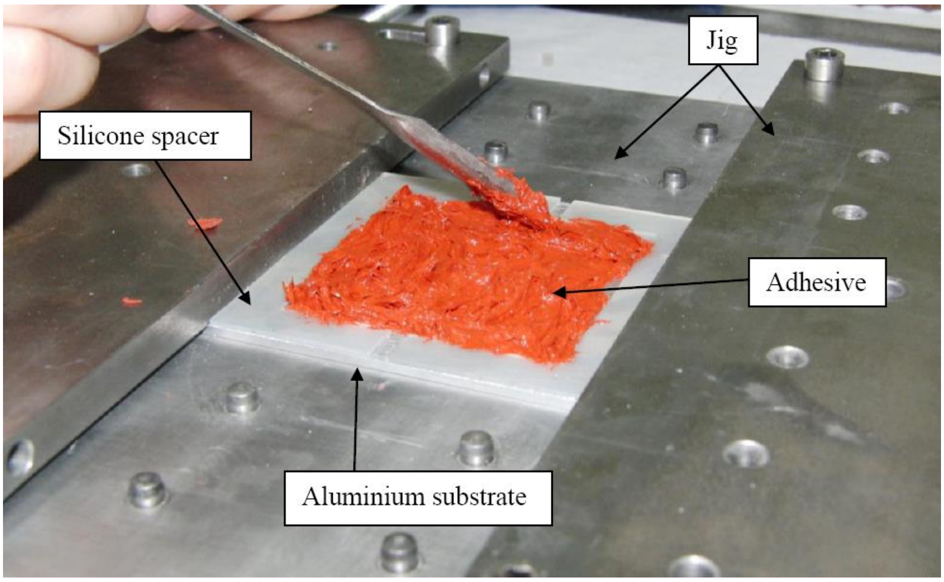

Figure 4- Adhesive application in the assembly jig

Before bonding, the substrates were prepared as follows: the aluminium substrate was sandblasted and degreased while the ceramic tile was dried at 150ºC and subsequently degreased. These steps are necessary to ensure a durable metal-ceramic bond [19]. To ensure the thickness and precise location of the adhesive layer, a 1 mm thick silicone rubber spacer was applied between the substrates. This spacer had a square, 60 mm wide cutout in the centre where the adhesive was applied. If a mixed adhesive joint was to be produced, the spacer had 3 cutouts instead, separated by a very thin strip of silicone rubber. One was located in the centre for the stiff adhesive and two others were located in the flanks of the specimen for the flexible adhesive. These cutouts ensured that the central epoxy section had an area of 40 mm x 60 mm, while the RTV sections each had 10mm x60 mm. After the adhesives were applied and the substrates bonded, the jig was placed in a hot plate press for 1 hour at 140ºC (in the case of the joints with XN1244) or cured at room temperature for 24 hours (in the case of joints using only RTV106). After this initial period, the silicone rubber spacers were removed from the joint. Joints with RTV 106 must still be left curing for a further 6 days until they achieve full strength and are ready to be tested.

2.3 Static testing at low and high temperature

This test procedure was intended to simulate the effect of a lateral force on the heat shield tile, a force such as an impact or the pressure created by very high speed airflow. The shear testing procedure was performed by mounting the specimens in a tool specially designed and built for this purpose, shown in Figure 5.

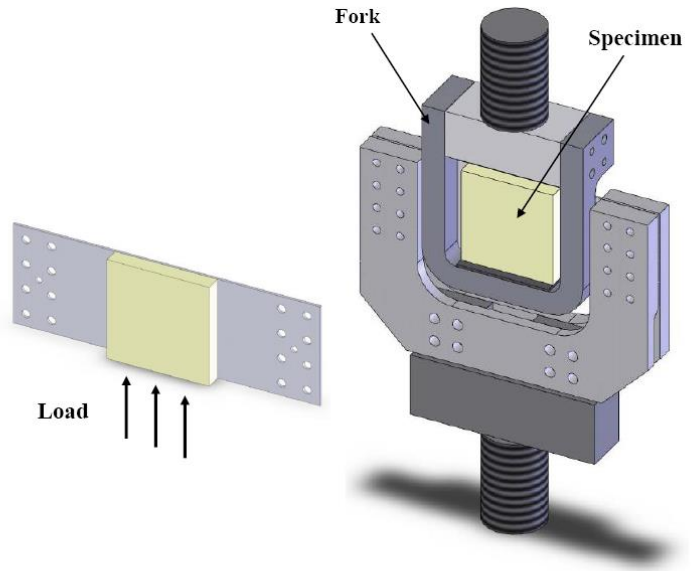

Figure 5 – Specimen (left) and shear testing tool (right).

The aluminium substrate of the specimen was laid horizontally and bolted with sixteen screws to a fork-like structure that could be pulled downward by an MTS servo-hydraulic machine 321.32 (MTS, Eden Prairie, MN, USA). In the upper section of the tool, the ceramic tile was secured inside a steel frame that did not allow it to move vertically. When the bolted aluminium substrate was pulled down by the test machine, the ceramic substrate could not move and this introduced a large shear load component in the adhesive layer. It is important to mention that a perfect shear loading is not achieved as the ceramic substrate still has some freedom to rotate due to the offset position of the applied forces, the thickness of the adhesive layer and the existence of some bending in the metallic substrate. The test tool could be easily modified to introduce a state of pure shear loading but this was decided against as it represents a departure from the actual practical application, where impacts in the ceramic can be demonstrated to produce peeling loads as well as shearing loads.

The mechanical tests were done in the MTS servo-hydraulic machine with two different speeds. 1 mm/minute was used for the RTV106 silicone adhesive and 0.5 mm/minute was used for the joints with XN1244 epoxy (mixed or single adhesive). This speed was chosen to regulate the duration of the test based on the expected displacement and to allow a better observation of the failure mechanisms of the brittle adhesive. While it is known that the test speed can have some influence on the test results, the small difference (0.5 mm/minute) was estimated not to have any perceivable influence on the final strength of the specimens.

Shear testing was not only performed at room temperature but also at high and low temperatures. For the high temperature tests, the heating was done by a flame directed at the ceramic surface using a pressurized gas burner to simulate the superheated air that flows over an actual heat shield. Heating power of the gas burners was adjusted to achieve a steady temperature of 100ºC in the adhesive layer. Thermocouples embedded in the adhesive layer were used to measure this value. When the adhesive layer was uniformly heated to 100ºC, the surface temperature in the ceramic was verified to be around between 600 and 700º C, measured with an infrared camera. This camera was also used to monitor the temperature distribution in the back of the specimen, as shown in Figure 6. A more detailed description of the heating system and its calibration can be found in Marques et al [9].

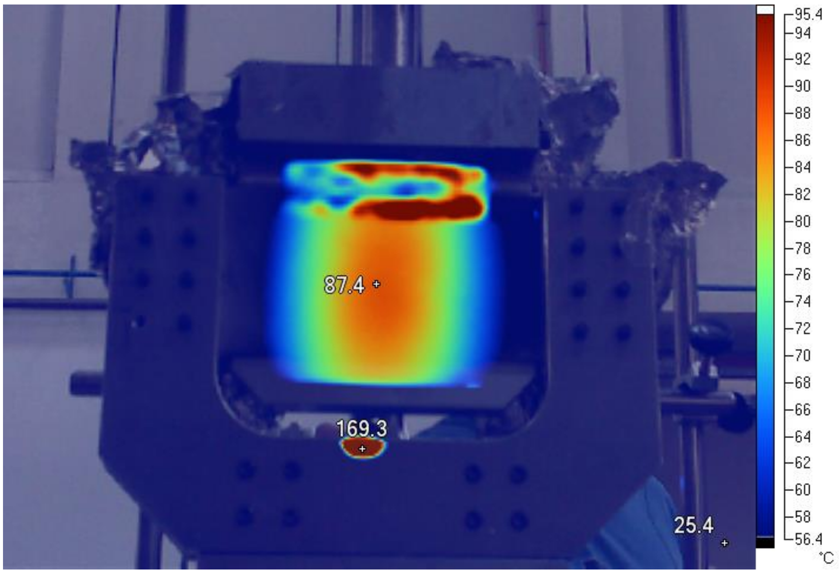

Figure 6 - Infrared image of the specimen rear plate

Mechanical loading was only performed when the temperature of the adhesive layer stabilized around 100ºC (+/- 5ºC). These values were controlled with a thermocouple installed in the geometric centre of the adhesive layer, at mid-thickness. Shielding was installed around the shear testing tool and the MTS hydraulic machine to ensure that the heat did not interfere with their usage.

Low temperature testing was performed in the same universal testing machine that was used for the room temperature and high temperature testing. A simple chamber, made of expanded polystyrene foam, was installed around the shear testing tool and filled with dry ice pellets. This chamber is shown in Figure 7. After sealing the door, the insulation kept temperature inside the chamber reasonably stable around -65º C. This temperature is defined only by the dry ice and insulation level as the chamber used does not possess any system to regulate the temperature. As was done in the high temperature tests, thermocouples were installed inside the chamber to monitor the temperature and ensure that an even temperature distribution exists.

Figure 7 – Chamber used for low temperature testing

At least three tests were carried out for each condition and type of specimen.

2.4 Impact testing at room temperatures

A drop weight impact testing machine was used for these tests, shown in Figure 8. This machine uses a winch system to pull a hammer upwards to a given height. Upon the operator's command, the hammer drops and hits an anvil, on which the specimen is assembled. A load cell measures the impact forces and displacements during the collision, as well as the vibration response of the specimen after the impact.

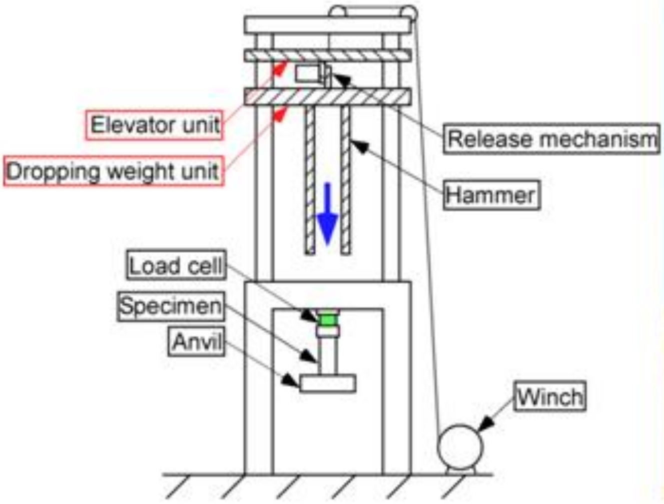

Figure 8 – Schematic drawing of drop weight impact testing machine (left) and image of the finished machine (right)

The machine had a specially designed anvil and specimen holder installed, to ensure compatibility with the specimen studied in this work. It is similar in construction to the tool used in the static shear testing procedure. Figure 9 shows the main components of this structure.

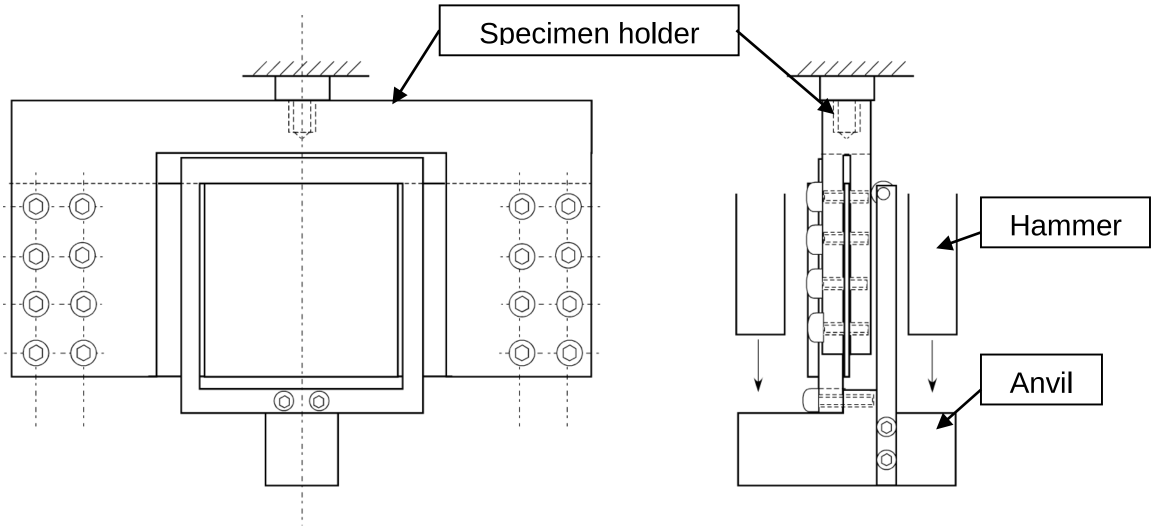

Figure 9 - Specimen holder and anvil for the impact tests

The hammer used in this test had a weight of 25 kg and reached a maximum velocity of 4 meters per second. This corresponds to an impact energy of 200 J. All impact testing was performed at room temperature.

3 Results

3.1 Static testing

The average failure loads for the static tests are presented in Figure 10,

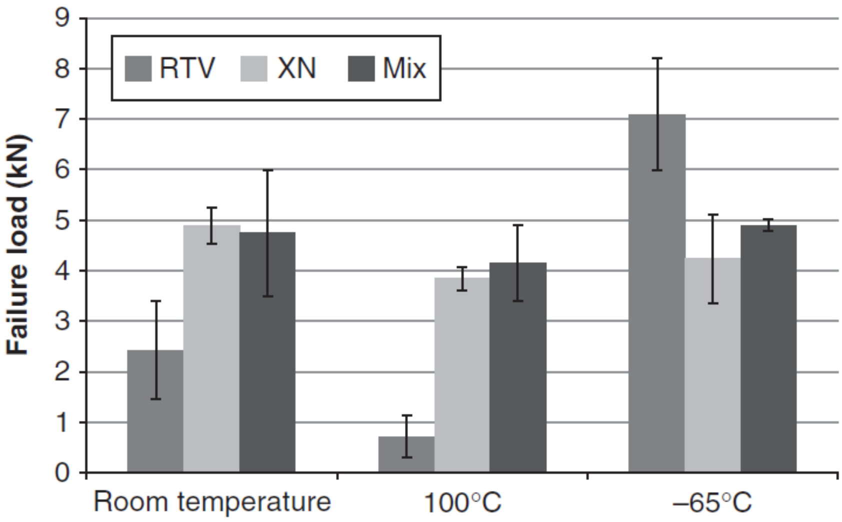

Figure 10 - Average failure loads during static testing for the three temperature levels

At room temperature, XN1244 epoxy is the best performing adhesive, with a slight advantage over the mixed joint. RTV106 silicone joints exhibit lower strength. At higher temperatures, RTV silicone joints lose a large percentage of strength; there is a reduction from 3 kN to slightly over 1 kN. In contrast, the mixed joint and the XN1244 joints have a less pronounced loss of strength. The strongest type of joint for these temperatures is the mixed adhesive joint.

At the lowest temperatures (-65ºC), the joint with RTV106 silicone excels, achieving the highest failure load registered at any temperature. The joint which uses a mixed adhesive layer surpasses the results of the joint containing only XN1244 adhesive as the portion of RTV106 presented in the joint takes over most of the load.

All of the joints, at the three temperature levels studied, failed cohesively. The joints using only RTV106 silicone had cohesive failure in the adhesive, while the joints that used XN1244 had cohesive failure in the ceramic substrate (this can be clearly seen in

Figure 11) This means that the upper limit for the joints that used XN1244 is not necessarily the adhesive itself but the resistance of the ceramic tile.

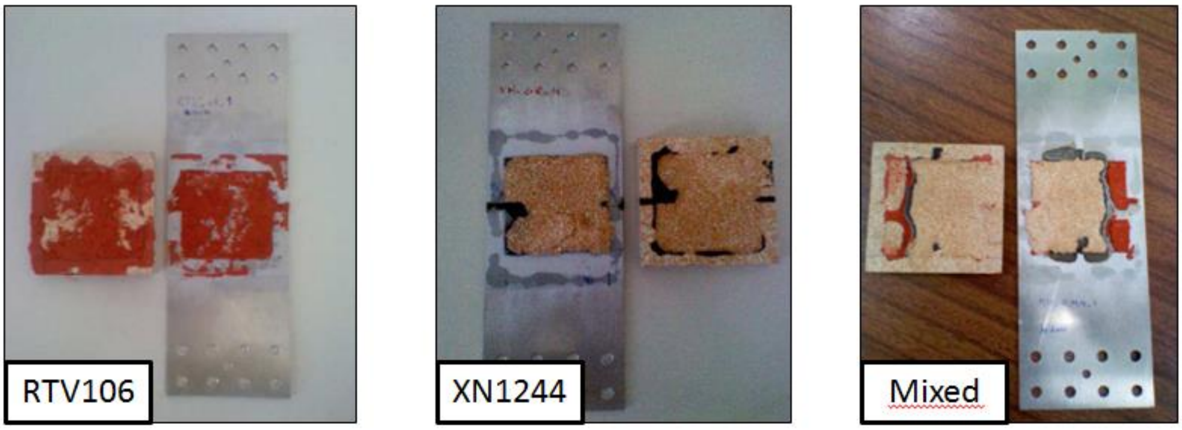

Figure 11 - Typical fracture surfaces found after static testing

The failure process of the ceramic tile is also different between joints. Joints fabricated using only XN1244 fail in a brittle and sudden manner, with the complete separation of the ceramic tile from the specimen. The joints that use RTV106 do not allow this type of failure mode. The ceramic tile is kept in position even when the adhesive layer has been deprived of most of its strength. This type of failure is especially useful for the intended application as the tile can still provide thermal insulation.

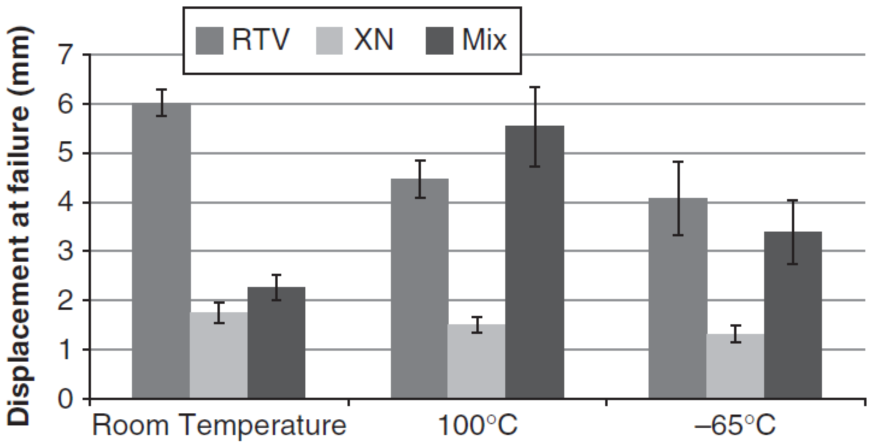

Figure 12 - Average displacement at failure during static testing for the three temperature levels

The progressive loss of strength of the mixed adhesive joints can also be inferred from the maximum displacements measured. As it can be seen in Figure 12, the presence of

RTV106 silicone in the mixed adhesive joints allows it to have a significantly higher displacement than the XN1244 joints at high temperature but also with higher strength. This is caused by progressive failure of the adhesive layer. This can be also seen in the force-displacement graphs registered during testing at high temperature, plotted in Figure 13.

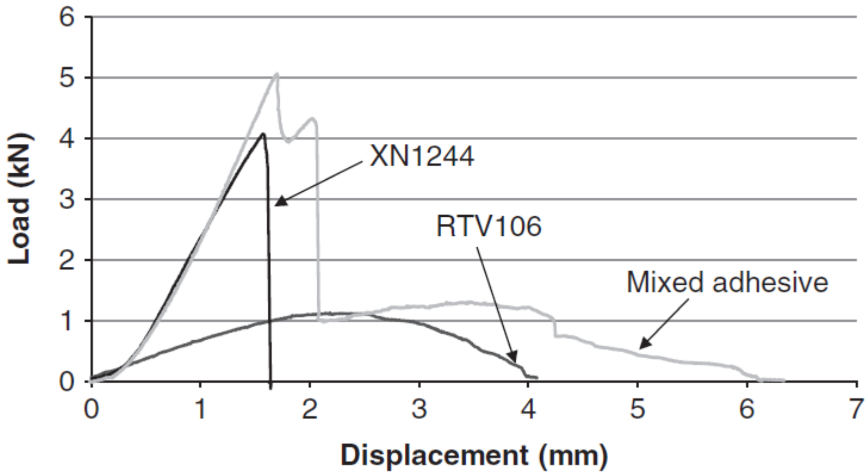

Figure 13 - Representative load-displacement curves for specimens at 100ºC

The progressive failure and peaks represent the transfer of load bearing from the strongest and stiffest epoxy centre section to the weaker and more ductile silicone outer sections. As different sections of the epoxy layer fail, we find a series of successive peaks in the load value. When the entire epoxy layer has been rendered incapable of carrying load, the silicone layers take over and lead to high values for maximum displacement to be achieved (comparable to those of RTV silicone alone), even after the ceramic tiles breaks. This phenomenon of progressive failure is not exclusive to the high temperature tests. Though the effect is less evident, Figure 14 demonstrates its existence at room temperature.

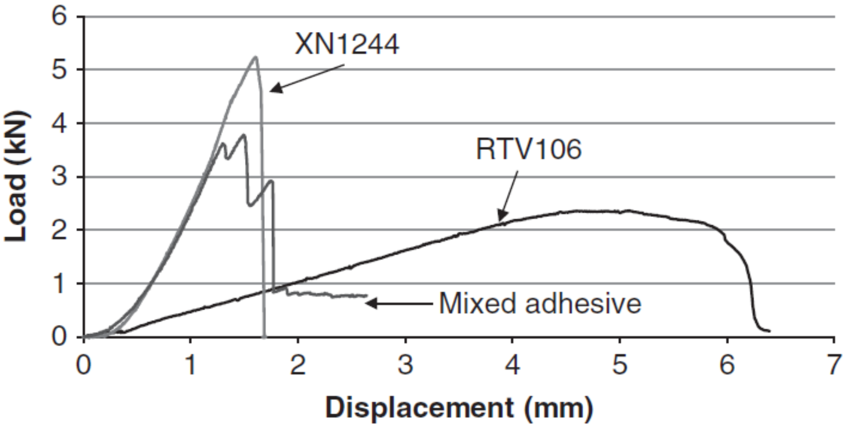

Figure 14 - Representative load-displacement curves for specimens at room temperature

At low temperature, Figure 15 depicts the typical behaviour of the three types of specimens. Here, the specimens using RTV106 silicone are shown to have high strength and displacement levels, improving on the two other configurations by a significant margin.

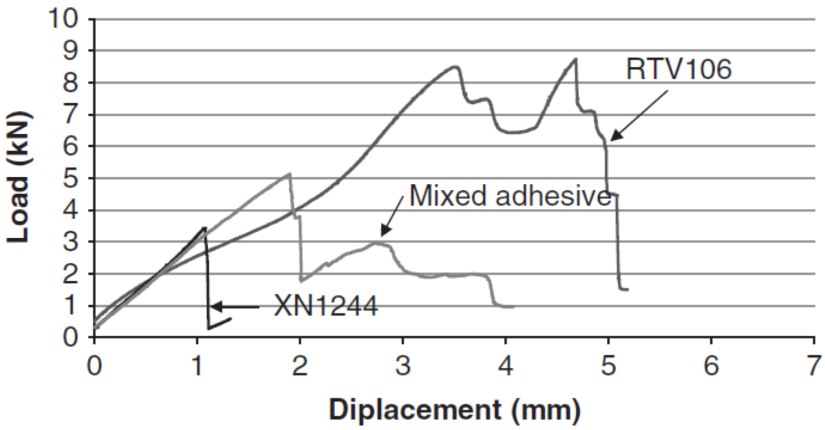

Figure 15 - Representative load-displacement curves for specimens at -65ºC

The energy absorbed is substantial, making this joint configuration the optimal solution if the joint is to be used only for low temperature applications. However, if we intend to develop a joint that will operate across a large envelope of temperatures, the RTV106 silicone alone does not exhibit satisfactory performance, mainly due to the reduced strength values at high temperature. Joints using XN1244 epoxy are very consistent in terms of maximum strength. However, they exhibit very small displacement in all cases, which translates into a reduced amount of absorbed energy. The mixed adhesive joint therefore appears in these tests as a very reasonable compromise, able to sustain high load values consistently, coupled with displacement values that guarantee a high level of energy absorption.

3.2 Impact testing

Figure 16 shows the results of the impact testing performed on the three types of specimens tested, combined with the results of the static tests at room temperature. All specimens exhibited a significant increase in failure load.

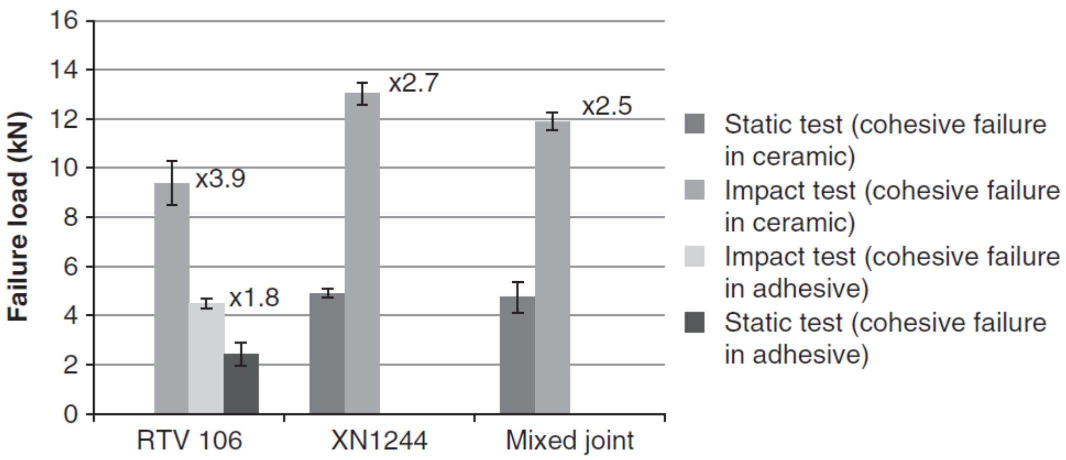

Figure 16 - Comparison of impact and static test failure loads for each specimen configuration at room temperature (improvement in strength over static testing indicated).

Specimens with solely XN1244 adhesive layer achieved the highest overall failure load values, with an increase of nearly 170%. Mixed adhesive joints had similar failure load values and comparable increase in strength using the static test results as reference. A study of the fracture surface, depicted in Figure 17, demonstrated that the failure always occurred in the ceramic substrate for these two specimen configurations.

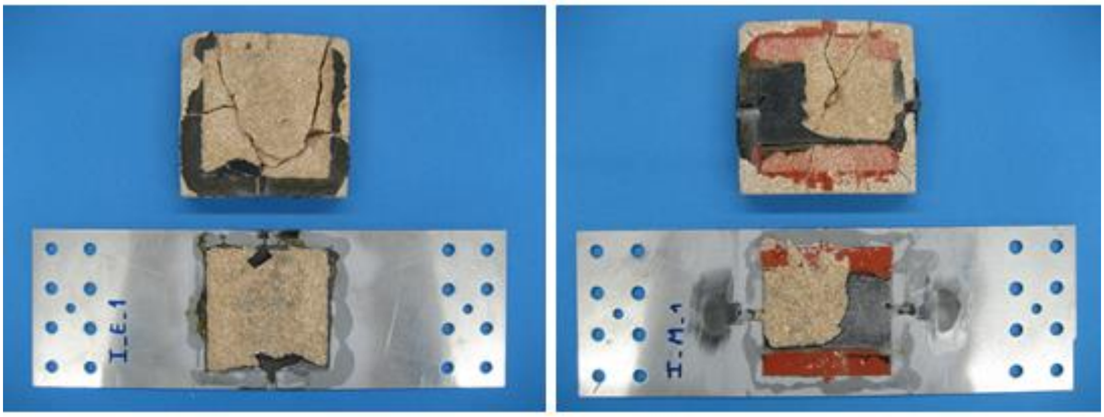

Figure 17 - Cohesive failure in the ceramic for XN1244 (left) and mixed adhesive specimens (right) tested at room temperature under impact

Analysis of impact test results of the specimens containing only RTV106 silicone is considerably more complex, as these specimens exhibited two distinct types of failure. While part of the specimens tested had cohesive failure in the ceramic substrate, verified in the two other configurations tested, another part of the specimens exhibited a cohesive failure in the silicone layer. The specimens with this type of failure exhibited extremely low failure loads. Figure 18 shows the two different fracture surfaces found in RTV106 specimens after impact testing.

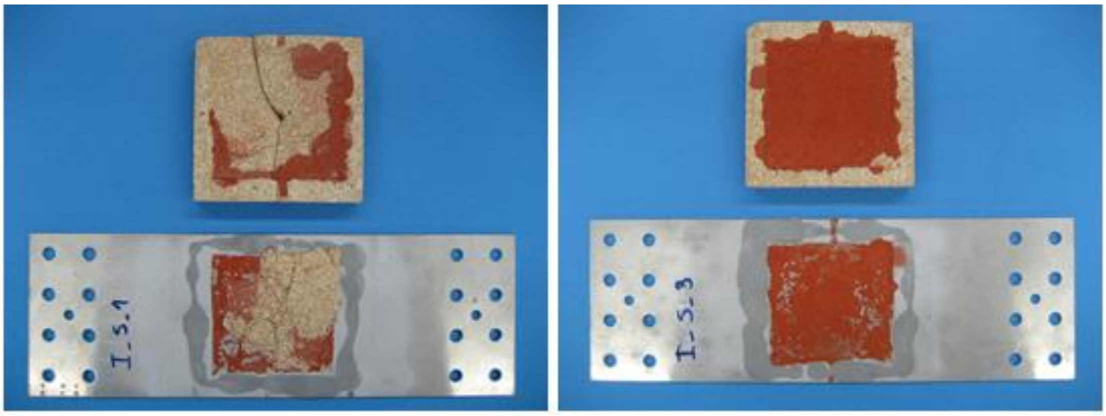

Figure 18 - Cohesive failure in the substrate (left) and in the adhesive (right) for RTV106 specimens tested at room temperature under impact.

RTV106 specimens which had cohesive failure in the adhesive had a relatively small improvement in strength over the specimens subjected to static testing (80% improvement) while the specimens which had cohesive failure in the ceramic substrate were able to withstand maximum impact forces nearing those of the XN1244 and mixed adhesive specimens, with an overall improvement of 290%. This division in the behaviour of the RTV106 specimens can, in part, be justified by the lengthy and difficult curing process of this adhesive. This adhesive requires contact with humidity to cure. Large areas, as the found under the ceramic tile in this specimen, always create problems in ensuring a complete curing in the central section, which is further from contact with ambient humidity. In contrast, in the mixed adhesive joints the RTV106 sections are located in the outer portions of the adhesive layer and cure faster and more thoroughly.

The difference between the static and impact testing results for the specimens that exhibited cohesive failure in the ceramic layer can be explained by the behaviour of the ceramic. These tests indicate the existence of a strain rate dependency for the cordierite used, as specimens under impact withstood a significantly higher force at failure. A brief explanation for the strain rate dependent properties of ceramics is as follows [20]. It is proposed that the presence of micro-cracks in the ceramic bulk is responsible for the time dependent properties of ceramics. During quasi-static loading cases, the micro-cracks act as discontinuities that reduce the load bearing capability of the ceramic as the fracture progresses unimpeded through these micro-cracks and along the bulk material. However, during impact testing the propagation of force is sufficiently fast to ensure that the micro-cracks are not a factor and the material fractures as a whole.

To support this explanation, a small complementary analysis of the strain rate sensitivity was performed in bulk specimens of cordierite, under three-point bending. These specimens were loaded in three-point bending according to the procedure based on the ASTM C 674 – 88 standard for testing ceramic materials. Two different loading speeds were used: a slow rate of 2 mm per minute and a faster rate of 500 mm per minute. 500 per minute is the upper limit of the testing machine used, but still several orders of magnitude slower than the 5000 mm per second of the actual impact tests presented before. The results are presented in Figure 19.

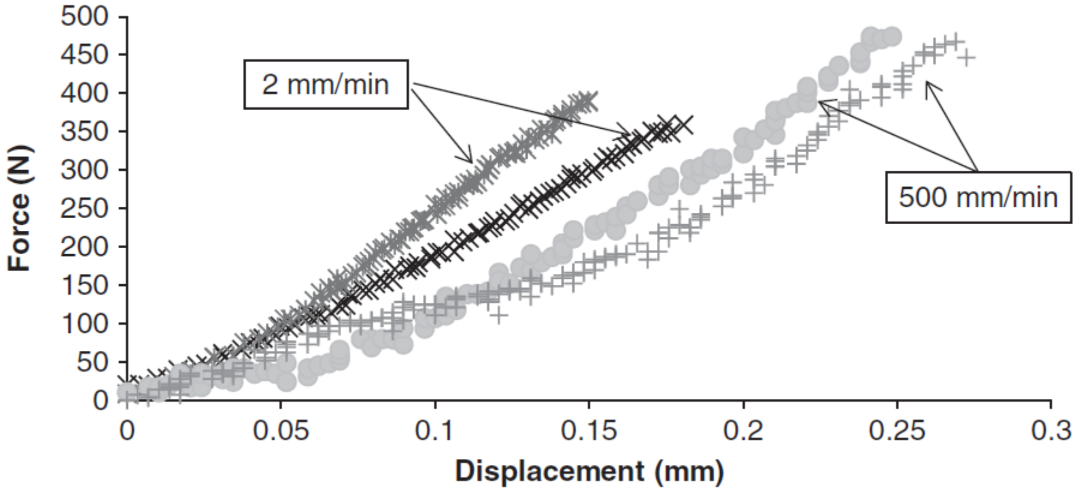

Figure 19 - Comparison of force-displacement plots for cordierite specimen subjected to two strain rates. Curves for two specimens at each strain rate are shown.

As predicted, the cordierite specimen exhibits a clear strain rate dependency. In this test an average increase of failure force of more than 30% was found.

Impact testing demonstrated that, for a heat shield using a ceramic tile, the impact resistance is mainly dominated by the properties of the ceramic. All three configurations performed similarly in terms of maximum strength achieved under impact.

4 Conclusions

The behaviour of a joint representative of an aerospace heat-shield was studied and tested with two different devices. One of the devices was used to produce failure under a shearing load at three different temperature levels. The other device subjected the specimen to impact testing at room temperature. Two different adhesives and a further additional combination of the two were used in the adhesive joint.

At room temperature, the highest static load was achieved by use of the XN1244 epoxy. This adhesive has much improved mechanical performance over the RTV106 silicone, with similar insensitivity to high temperatures. At low temperatures, RTV106 silicone joints were demonstrated to sustain extremely high loads. The specimens produced with a mixed adhesive layer were shown to have consistent strength levels in both low and high temperature conditions. Regarding static strength, their behaviour is equivalent to the behaviour of XN1244 epoxy specimens.

Due to consistent cohesive failure in the ceramic substrate, the XN1244 epoxy joints and mixed adhesive joints are limited not by the strength of the adhesive layer but by the strength of the ceramic. This explains the similarity in failure loads during static testing. These two type joints exhibit considerably improved shear strength over the RTV joints at high temperatures and room temperatures.

Mixed adhesive joints kept their strength at 100ºC while the RTV silicone joints exhibited a large drop in strength. Compared with XN1244 joints, they also achieved this strength with much more displacement at both low and high temperatures. This can be considered an improvement in energy absorption capability. It was also found that joints containing RTV106 silicone do not release the ceramic tile during tests. This means that even if the adhesive layer is damaged, the ceramic tile might still be able to shield the structure effectively.

All three joint configurations tested have exhibited an increase in failure loads under impact. Joints with XN1244 epoxy exhibit the highest failure loads. Joints with RTV106 exhibit the highest strength gain, providing that that the failure starts in the ceramic tile. The ceramic tile exhibits significant sensitivity to strain rate and is one of the most important factors in the overall joint strength.

Overall, mixed adhesive joints were shown to be a capable alternative to RTV silicone joints for this application. While RTV silicone joints offer the highest failure load at low temperatures, the mixed adhesive joint provides greater static loads at the other temperature levels studied, impact test strength similar to the epoxy joints and an increased displacement at failure. Therefore, by bonding a heat shield with a mixed joint of the type described in this paper, consistent static and impact strength along the temperature range can be expected.

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Testing and simulation of mixed adhesive joints

Testing and simulation of mixed adhesive joints for aerospace applications

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Abstract

An important aerospace application of adhesives is in heat shields intended to protect metallic structures from heat. Heat shields ceramic tiles are bonded with a room temperature vulcanizing silicone adhesive, which has high temperature resistance but low strength. Previous works proposed mixed adhesive joints as a viable solution, therefore an investigation of this technique was performed.

This work studies three adhesive joint configurations: joint with RTV silicone only, joint only with high temperature epoxy and a joint introducing both adhesives in the same joint (mixed joint). The aim of the research was to simulate the load on a heat shield and predict the joint strength. Finite element models were developed using a triangular cohesive law including initiation, softening and failure. Numerical results were compared with experimental results. Properties of the ceramic were obtained with an inverse method. There was a good agreement between experimental and numerical data, showing that this technique could be used for load prediction and optimization of this type of models.

K**eywords:** Dual adhesive joints; High-temperature adhesives; Low-temperature adhesives; Cohesive elements;

1 Introduction

There is significant difficulty in bonding ceramic to metals for high temperature aerospace applications. This is due to various reasons, such as the large difference in properties of the two substrates, the demanding environmental conditions and the large temperature gradients. The mixed adhesive joint technique has been proposed as a good solution for this problem and therefore its use in this application is analysed during the course of this paper. The concept of mixed adhesive joints was first proposed in 1966 by Raphael [1]. With careful selection of the adhesives used, there is a possibility to reduce the stress concentration at the ends of the overlap, typical for single lap joints and which can reduce premature joint failure. A flexible adhesive should be present at the ends of the overlap, while a stiff adhesive is applied in the central section of the joint, where it will be less subjected to large deformations under loading. In 1973, Hart-Smith [2] recognized that the use of mixed adhesive joints could yield improvements in the mechanical strength of joints subjected to large temperature gradients. In 2007, da Silva and Adams [3] made use of this concept and predicted improvements in the mechanical behaviour of a joint under a large temperature gradient. In their approach, the adhesives to be combined were not only dissimilar in the mechanical properties, but also in their temperature handling capabilities. The stiffer adhesive was also a high temperature adhesive (HTA), responsible for the joint strength when the joint is subjected to heat while the more flexible adhesive was now a low temperature adhesive (LTA), carefully selected to be able to provide strength to the joint under negative temperatures. At higher temperatures, a high-temperature adhesive (HTA) in the middle of the joint retains the strength and transfers the entire load while a low-temperature adhesive (LTA) is the load bearing component at low-temperatures, making the HTA relatively lightly stressed. At low-temperatures, the load must essentially be supported by the LTA. If its modulus is of the same order as the modulus of the HTA, most of the load will be carried by the LTA. However, if its modulus is much lower than the modulus of the HTA, then there might still be a considerable load in the HTA. Therefore, the geometry and ratios between LTA and HTA must be carefully studied to improve the behaviour over a joint composed only of HTA. Figure 1 illustrates the working principle of this type of joint. In 2007 [4], da Silva and Adams presented experimental data that supported these conclusions, proving the concept for a temperature range of -50 to 200ºC with titanium and CFRP adherends.

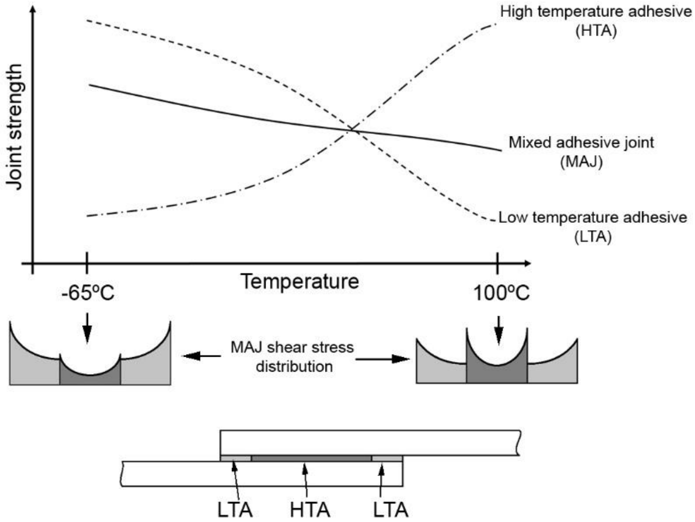

Figure 1- Working principle of the mixed adhesive joint concept.

Marques et al [5, 6] performed a series of experimental studies, bonding ceramic tiles to a metallic substrate using a mixed adhesive joint, combining a RTV silicone with a high temperature epoxy. The joints were tested under shear at room temperature, -65ºC and 100ºC. With these static tests, mixed adhesive joints were found to have consistent strength at high and low temperature, while providing a good amount of joint displacement in both cases. Impact tests were also performed and again the mixed adhesive joint was demonstrated as a good alternative to the use of a single adhesive, able to handle large failure loads.

Cohesive zone models (CZM) are increasingly being used to improve the failure load prediction of finite element models and various authors such as Needleman [7], Tvergaard et al [8] and Camacho et al [9] early adapted this technique for use in adhesive joints. A CZM is able to represent the fracture process and location, advancing beyond the typical continuum mechanics modelling. It does this by including in the model a series of discontinuities modelled by cohesive elements, which use both strength and energy parameters to simulate the occurrence and advance of a fracture crack [10, 11]. This technique is especially useful for adhesives, as they present a discrete zone, the adhesive layer, where failure can be expected and therefore can be easily modelled. While initially this type of element has overlapped nodes during the elastic portion of loading, when degradation of the element finally occurs the nodes start to separate and stop providing transmission of load in the model, therefore acting as a real crack in the material.

The parameters needed for the simulation can vary as well as the methods used to determine them. In this type of models there is an underlying relationship between the stresses and relative displacements of the nodes of a cohesive element. This relationship between the stresses and displacements is governed by a traction separation law, which can be shaped to better suit the behaviour of the material or interface being simulated. Figure 2 shows such a traction separation law, where t_n *and* t_s are the yield stresses, δ_n^0 and δ_n^0 are the yield deformations and δ_n^f and δ_n^f are the deformations at failure.

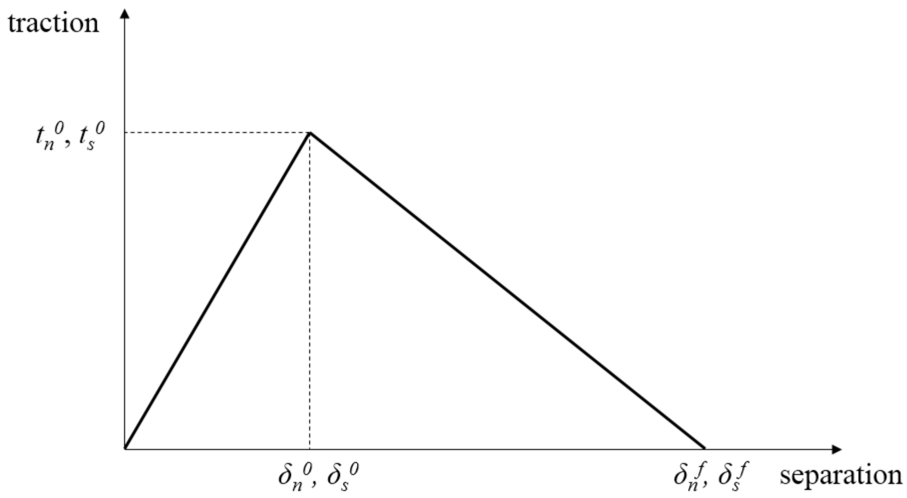

Figure 2 - Traction-separation law with linear softening

The shape of this law can be changed to more adequately fit the mechanical behaviour of the simulated material. The initial elastic portion is always kept linear, but the in the literature various shapes for the softening portion of the curve can be found. Needleman introduced a shape based on more complex functions such as polynomial [7] and exponential [10] laws. Tvergaard and Hutchinson [8] suggested a trapezoidal model while Liljedhal [11] et al proposed the simpler bilinear model. There is however not a consensus regarding the importance of the softening law shape. While some reasearchers [8, 12] have determined that the shape of this portion of the law is not critical for the results accuracy, others have found the opposite effect [13-15]. Chandra et al [15] have published a report and review of the various CZM laws available in the literature. This work therefore aims to increase the understanding of the mixed adhesive joint capabilities, by mechanically testing metal-ceramic specimens at room temperature and under shear loading and then using this information to allow the construction and validation of a finite element model. To more accurately represent the real joint, the model makes use of cohesive elements, combining a continuum mechanics approach with a fracture mechanics approach. The cracks can therefore be simulated and matched to the cracks identified on the mechanical testing and this process leads to a validated model that can be used for joint optimization purposes.

2 Experimental details

2.1 Materials

Two different adhesives were selected, a stiff and relatively brittle high temperature epoxy of the XN 1244 type, supplied by Nagase Chemtex, (Osaka, Japan) and a very flexible and ductile RTV106 silicone rubber supplied by ACC Silicones LDT (Bridgewater, UK). The RTV silicone, RTV106 was selected for this experimental procedure. This type of acetoxy silicone is extensively used in high temperature applications. This one-part adhesive is known for its high temperature resistance but exhibits very little mechanical strength when compared with most structural adhesives. The curing process of the RTV106 adhesive is based in the absorption of humidity from the air [16] and, to ensure a complete cure, the water molecules must diffuse from the surface of the material to the interior. This makes the cure a slow process, especially when thick layers of adhesive are used, and 10 days are usually needed to ensure complete cure in the larger adhesive layers. The epoxy adhesive, XN 1244 is a one component, high temperature, paste epoxy adhesive, with a high glass transition temperature, providing good mechanical properties up to 150ºC [17]. This adhesive has a thermal based curing process, requiring temperatures around 140ºC during 1h for complete cure. Table 1 lists both adhesives mechanical properties at room temperature, as obtained by Banea et al [17-22].

Table 1- Mechanical properties of RTV 106 silicone and XN1244 epoxy at room temperature [17-22]

	RTV106 silicone	XN1244 epoxy
E - Young’s Modulus (N/mm^2)	1.6	5870
G - Shear Modulus (N/mm^2)	0.86	2150
t_n^0 - Tensile Strength (N/mm^2)	2.3	68.23
t_s^0 - Shear Strength (N/mm^2)	1.97	37
G_n^c - Mode I fracture energy (N/mm)	2.73	0.47
G_s^c - Mode II fracture energy (N/mm)	5	2.2

An aluminium alloy of the type 6063 T6 was selected as the metallic adherend of the specimen, to be shielded by a cordierite ceramic block. Cordierite is a ceramic material with high temperature resistance, able to withstand large temperature gradients and commonly used in oven liners. While pure silica is used as the shielding material for many aerospace applications, it was not readily available and therefore cordierite was selected as replacement with similar properties. Regarding the mechanical properties of cordierite, it was not possible to find complete and accurate data in the literature. A novel specimen was proposed for use in an inverse method of mechanical property characterization. This procedure is described in the numerical analysis portion of this work.

2.2 Specimens and manufacture

The ceramic tiles had a dimension 80x80x12.8 mm and were produced by water-jet cutting of a larger plate. They were bonded to the centre of the aluminium sheet using three different configurations of adhesive layers. One of the layers contained only silicone adhesive, other had only epoxy and another combined them both into a mixed adhesive joint. The specimen configurations and geometry are shown in Figure 3.

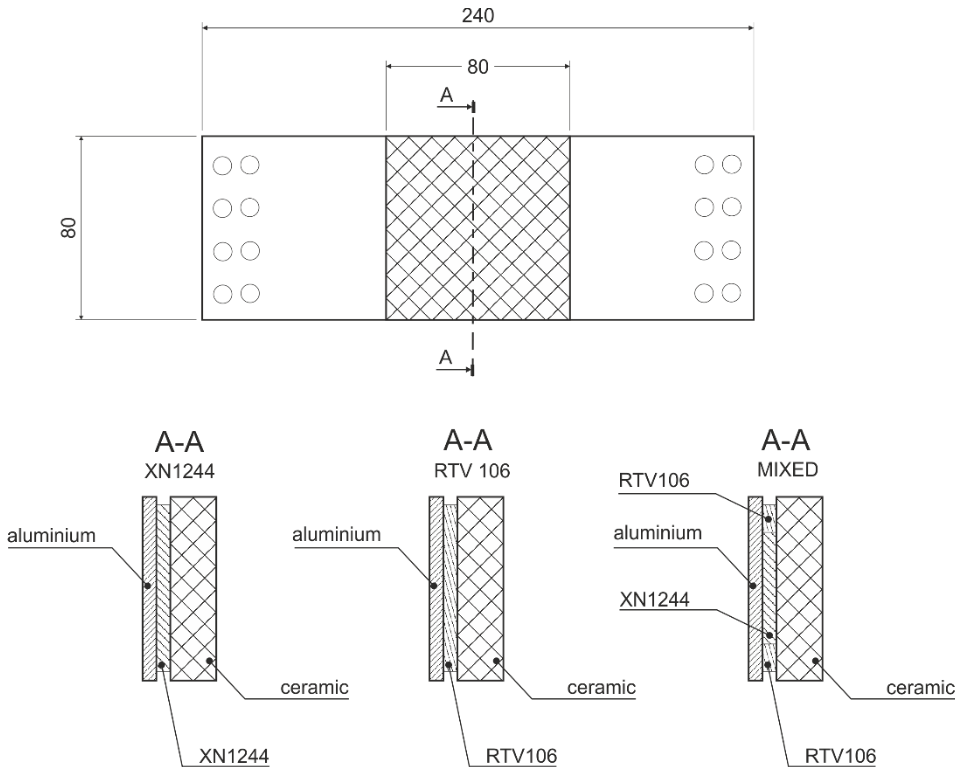

Figure 3- Specimen configurations and respective geometries (dimensions in mm)

A large adhesive thickness (1mm) was used to ensure strength of the RTV adhesive. While theoretically a thinner adhesive layer would provide higher joint strength improvements in comparison to a single brittle adhesive (because the load would be more concentrated at the ends of the overlap), in practice the use of RTV silicone in thin layers results in very weak joint strength due to its extremely low modulus of elasticity. A frame of silicone rubber, 1 mm thick, was cut to constrain the adhesive underneath the ceramic tile and also to set the adhesive layer thickness. Two different techniques were used to manufacture the single adhesive joints and the mixed adhesive joints. The latter type, instead of having an internal square of 60x60 mm^2, presents two thin barriers between the adhesives to obtain three different bonding areas and avoid the contact between the two different adhesives.

The silicone rubber frame needs to be first bonded with a small amount of cyanoacrylate adhesive to the metallic substrate in order to guarantee that it does not move sideways upon the application of pressure. A custom mould (shown in Figure 4) was built to guarantee the correct location of the parts during the curing process.

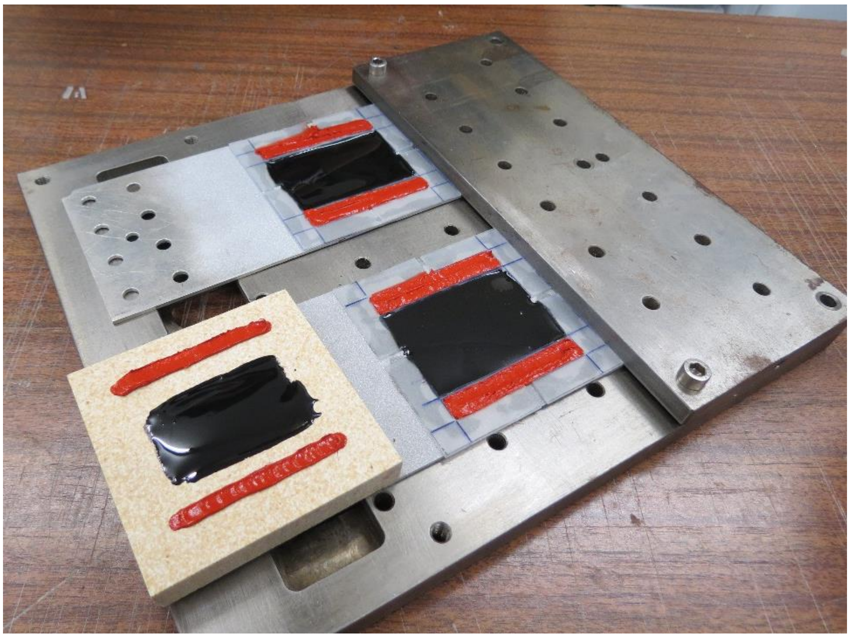

Figure 4 - Specimens in the mould, ready for bonding.

2.3 Static testing procedure

The specimens were tested in an INSTRON (Norwood, MA, USA) model 3360 electromechanical testing machine with a load cell of 30 kN. The test speed was 1 mm/min and the test was performed at room temperature. Four specimens were tested for each configuration. A custom testing tool was used to connect the components and specimen to be tested. It consists in two grips, with the respective adapters. Figure 5 shows a drawing of the tool with a specimen assembled.

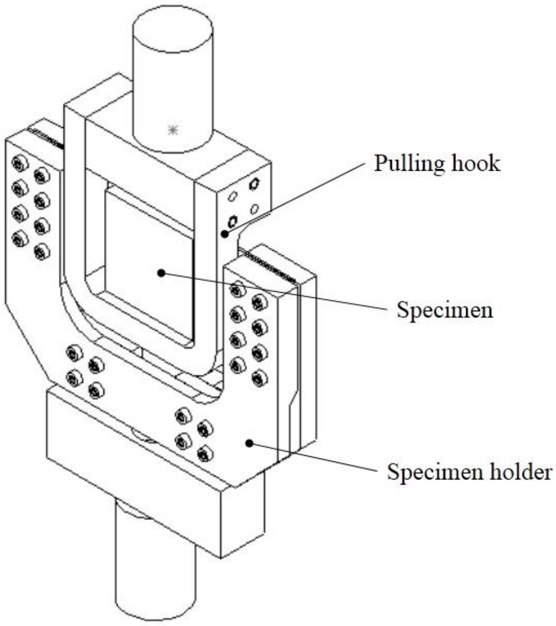

Figure 5- Illustration of testing tool and specimen.

The aluminium adherend is fixed to the base frame by a specimen holder and fastened by screws across the holes. The ceramic tile is sheared up by the motion of the crosshead, connected to the tile by the pulling hook. This component is manufactured in steel and for simplicity of assembly can be split in two separate parts. In addition to the testing machine load cell and the crosshead position sensor, two additional LVDT (linear variable differential transformer) sensors were also used to monitor the lateral displacement of the aluminium. Due to the configuration of the specimens and the testing tool developed, the shear test could be easily performed. The load-displacement curve (P-δ curve) was plotted during the test and a variety of properties regarding the whole specimen were determined: stiffness by the slope of the curve in the elastic zone, the maximum load P_{max}, and the maximum displacement δ_{max} at failure. Moreover, due to some degree of rotation of the specimen, extra equipment to measure the displacement was added. Two LVDTs were placed behind the test machine, and supported by a mechanism which allowed their translation in the vertical and horizontal axis for precise location. Two specific points on the back side of the substrate were selected and kept in contact with the LVDT shafts. As shown in Figure 6, they were located exactly in the medium cross section where the highest displacement of the metallic substrate was expected to occur. The output obtained is extremely useful to determine the right boundary condition of the model during numerical simulation.

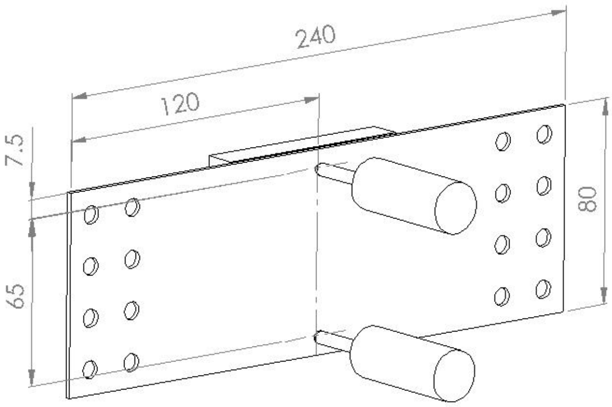

Figure 6 – LVDT sensor locations (dimensions in mm)

3 Numerical procedure

The finite element program Dassault Systèmes ABAQUS® (Vélizy-Villacoublay, France) was used to study the adhesive joint, using a cohesive zone model to model the crack propagation in the specimens. The cohesive element used for this purpose was one available in the ABAQUS® default element library for 2D models, of the COH2D4 type. This is a 4-node two-dimensional cohesive element. This element allows the use of a traction separation law with linear softening. While in an initial phase of this research work a 3D finite element model (FEM) was created and tested, it was considered to be excessively complex and room for simplification was found to exist. The 3D model was then replaced by a 2D finite element analysis of the specimen subjected to a shear load. This reduced model was viable with a good understanding of the boundary conditions. The analysis consisted in two steps. In the first step, a linear elastic analysis was carried out to adjust the boundary conditions. In the second step, full cohesive models were developed. Experimental results were then used to assist in the validation of the numerical models.

3.1 Determination of ceramic mechanical properties

A variety of different failure mechanisms on a bonded joint can occur. In order to predict the failure mode when the failure happens in the ceramic, knowledge of the mechanical properties of the cordierite used are fundamental. Due to the lack of mechanical property values of cordierite in the literature, the mechanical properties of ceramic tile had to be calculated by an inverse method.

As the ceramic tile is loaded in shearing mode, it is most important to study the properties regarding this type of loading. A novel specimen was designed for this purpose. To design this model, a finite element elastic model was first created in order to study the shear loading along a thin central section. Central cuts were designed and optimized as to ensure that shear loading was by far the most significant type of loading present. The specimen was then produced by water-jet cutting from a block of cordierite and then tested under compression. The specimen's shape is very similar to a TAST (Thick Adherend Shear Testing) [23] specimen, in which the central portion geometry is designed in a way as to create a pure shear loading when the specimen is compressed between two metal plates. The final specimen, as well as the tool used for its test can be seen in Figure 7.

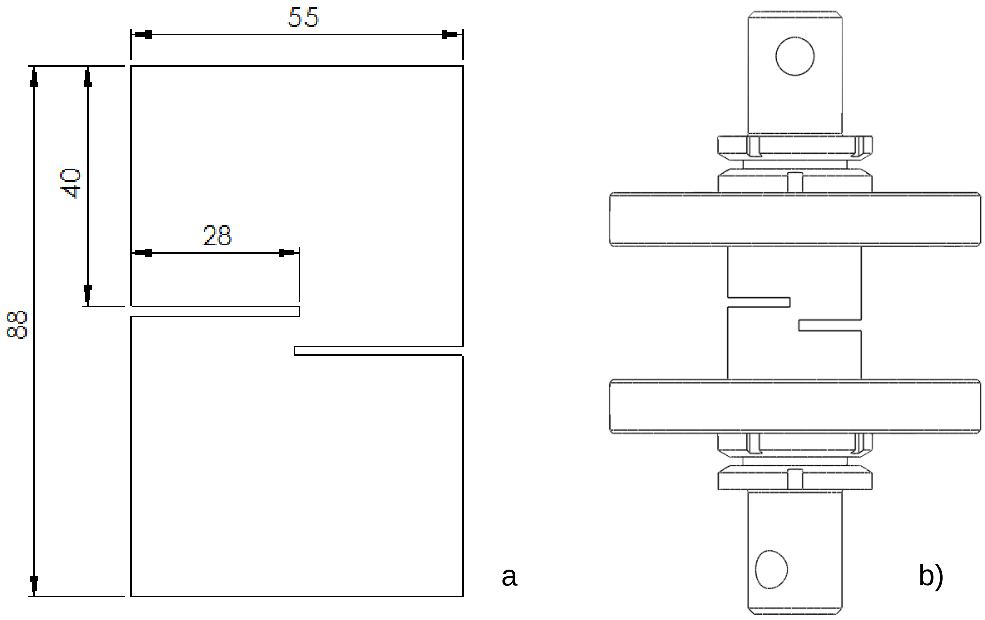

Figure 7- a) Specimen geometry (dimensions in mm); b) testing tool and specimen

After this process, a more complex model, including cohesive elements in the central section (where failure occurs) was built. By means of an inverse method, it was possible to estimate the cohesive properties of the specimen under shear loading conditions, simply by adjusting the properties until there was a good match between the simulation P-δ curves and the actual experimental curves

b)

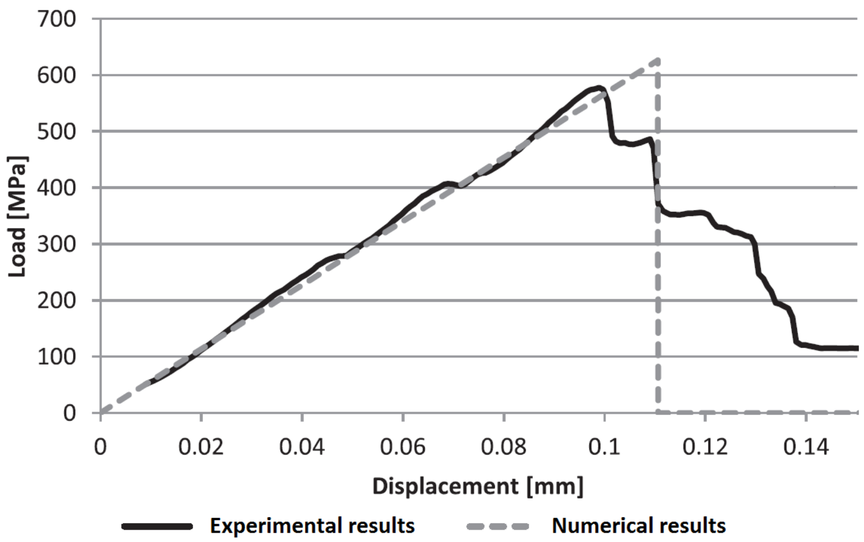

Figure 8 - Experimental and numerical load displacement curves for ceramic specimen

The properties of the ceramic material obtained via this inverse method are given in Table 2. These properties were incorporated in cohesive elements as a bi-linear material.

Table 2 - Mechanical properties of cordierite as determined by experimental/numerical matching.

	Cordierite
E - Young's Modulus (N/mm^2)	5200
G - Shear Modulus (N/mm^2)	2060
t_n^0 - Tensile Strength (N/mm^2)	45
t_s^0 - Shear Strength (N/mm^2)	45
G_n^c - Mode I fracture energy (N/mm)	0.5
G_s^c - Mode II fracture energy (N/mm)	0.5

3.2 Shear loading specimen models

FEA models were created for each type of joint configuration: adhesive layer with silicone (silicone joint), adhesive layer with epoxy (epoxy joint) and adhesive layer with dual adhesives (mixed joint). For each of these three configurations, linear elastic and cohesive analysis were separately performed. The initial elastic analysis was performed in order to adjust the boundary conditions. For the cohesive models, thin layers of cohesive elements were placed in the middle of elastic elements and the model was simulated until complete failure.

The boundary conditions for the finite element model were selected by studying each case. The main problem to be solved consisted of reproducing the displacement of the aluminum adherend in the cross section considered. Simple displacement and rotation restrictions, commonly used in most models were found not to be able to represent the amount of displacement present in the joint during experimental tests. To accurately represent the displacement of the full joint under load, it was proposed to connect two spring elements with carefully adjusted stiffness in two points of the aluminium substrate. In an ABAQUS®/Standard analysis it is possible to define springs that connect points to ground and exhibit the same linear behaviour independently of field variables. The configuration used for the boundary conditions is shown in Figure 9.

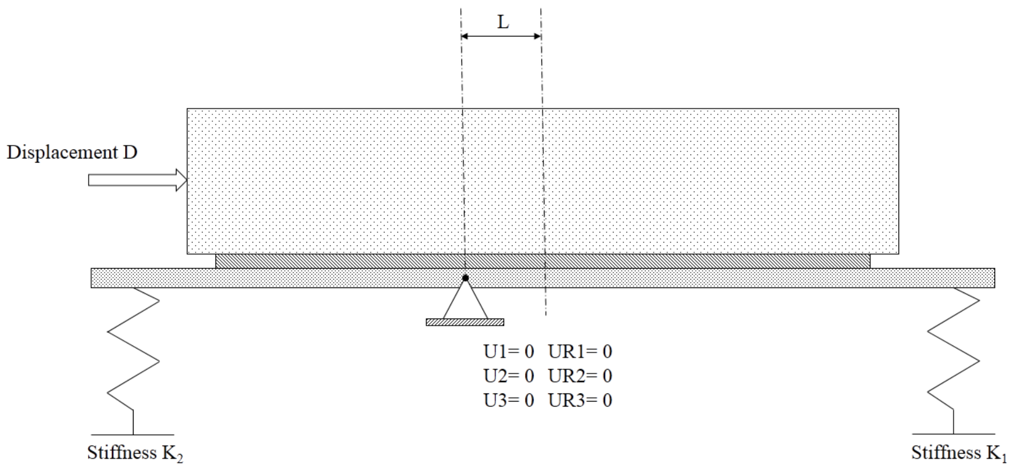

Figure 9 - Boundary conditions for the numerical model

The parameters defined were the position (selection of the points to connect to ground), the direction (to specify an orientation for the springs using a datum coordinate system) and the spring stiffness. To determine the spring parameters, some additional information about the displacement of the joint during the experimental test was required. As mentioned in the section detailing the experimental procedure, it was decided to instrument the experimental specimens with LDVT sensors (displacement sensors) in order to obtain curves which show the variation of displacement of the specimen in relation to the force applied. By adjusting the stiffness of the springs, these curves can be matched with the model ensuring that the boundary conditions are adequate.

However, the springs by themselves are not able to resist lateral forces so it was necessary to include another boundary condition to limit the lateral and vertical movement of the specimen. A “pinned” type of boundary condition restricts the *x* and *y* movement of the specimen while providing a hinge for the springs to actuate on. With these boundary conditions in place and comparing with the LDVT data, the spring stiffness values were found are presented in Table 3.

Table 3 - Spring parameters and locations for numerical models

Parameters	D [mm]	K_1 [N/mm]	K_2 [N/mm]	L [mm]
Silicone	8	80	75	20
Epoxy	2	1	450	7
Mixed	2	1	450	7

After the boundary conditions were satisfactory determined, the cohesive element models were developed. The main challenge in the construction of these models is the location of the cohesive element layers, which must be located in the areas where failure is expected. Figure 10 shows a schematic with the location of each layer for the two main types of specimens.

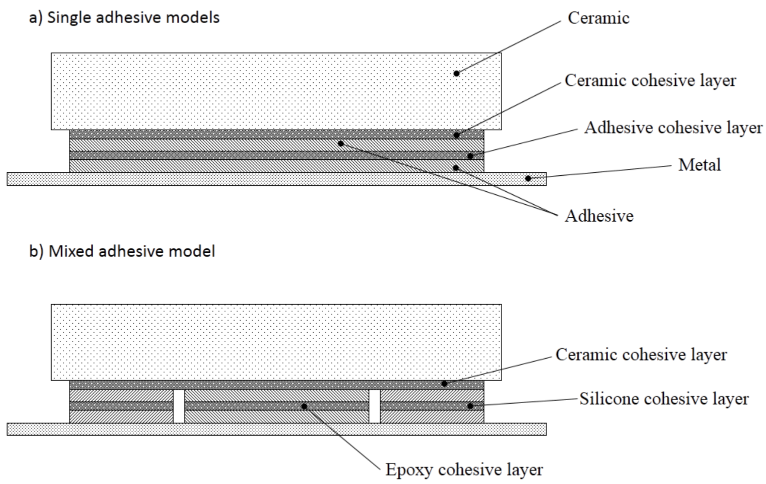

Figure 10 - Location of cohesive layers in finite element models (dimensions exaggerated).

The model of the joint containing silicone adhesive has two different layers of cohesive elements (Figure 10a). A layer is introduced in the bottom portion of the ceramic tile and the middle of adhesive layer. The thickness of the cohesive layers is 0.1 mm, much thinner than the actual adhesive layer thickness which is 1 mm. This low value is necessary to correctly use the cohesive elements as is also the same thickness present in the models and specimens used to determine the ceramic properties. This ensures consistency in the use of cohesive elements. The model of the joint containing epoxy adhesive (also Figure 10a) is similar, a thin layer of cohesive elements was placed in the middle of the adhesive and another layer of cohesive elements was located in the ceramic tile, immediately above the bonding line.

The configuration of the cohesive model for the mixed adhesive joint (Figure 10b) is the most complex as it has four different cohesive element layers. There is a layer for the lower portion of the ceramic, one in the middle of the epoxy adhesive and two additional layers located in the middle of each silicone section. This geometry allows the cracks to propagate in each of the adhesives and also in the ceramic.

4 Results discussion

4.1 Fracture surfaces

Figure 11 shows the typical fracture surface of a specimen containing only silicone adhesive. These specimens exhibited a generally cohesive failure of adhesive layer. A few zones with adhesive failure could be identified but were never substantial in area. The finite element model for this specimen translated the phenomenon correctly. Of the two cohesive layers in the model (ceramic and adhesive) only the layer placed in the adhesive was subjected to failure.

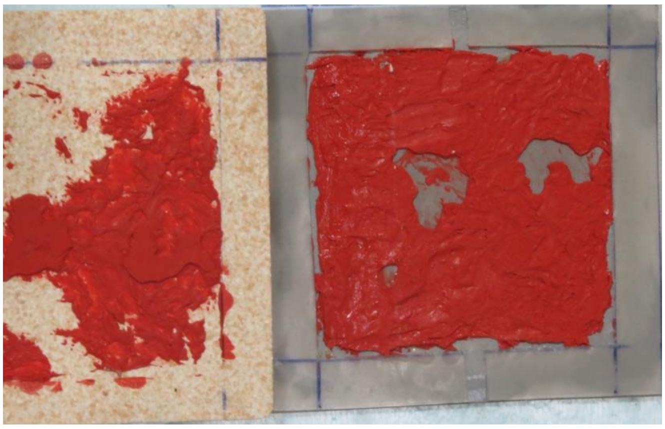

Figure 11 - Fracture surface of a specimen containing only silicone

Figure 12 shows the fracture surface of a specimen containing only epoxy adhesive. There is a purely cohesive failure of the ceramic material in the bonded area. This fracture is very near the adhesive layer. Again, the cohesive model used for this purpose was found to also have avoided failure of the adhesive and progressed only in the cohesive layer set in the ceramic material.

Figure 12 - Fracture surface of a specimen containing only epoxy

Figure 13 shows the typical fracture surface of a mixed adhesive joint. These specimens simultaneously exhibited cohesive fracture in the ceramic and the silicone layer. The initial crack was found to occur in the ceramic (similarly to the epoxy specimens) and then progressed into a cohesive failure of both silicone portions. This behaviour was also successfully modelled. In the models the crack progresses completely through the cohesive layer installed in the ceramic and then jumps to the cohesive layer installed in the silicone. The cohesive layer for the epoxy is left undamaged.

Figure 13 - Fracture surface of specimen with mixed adhesive layer

4.2 Numerical-Experimental curve comparison

The failure load results obtained in experimental testing are shown in Figure 14. To provide some information about the variation of the mechanical properties, experimental results for high temperature and low temperature are also provided. These results were already previously published by the authors [5].

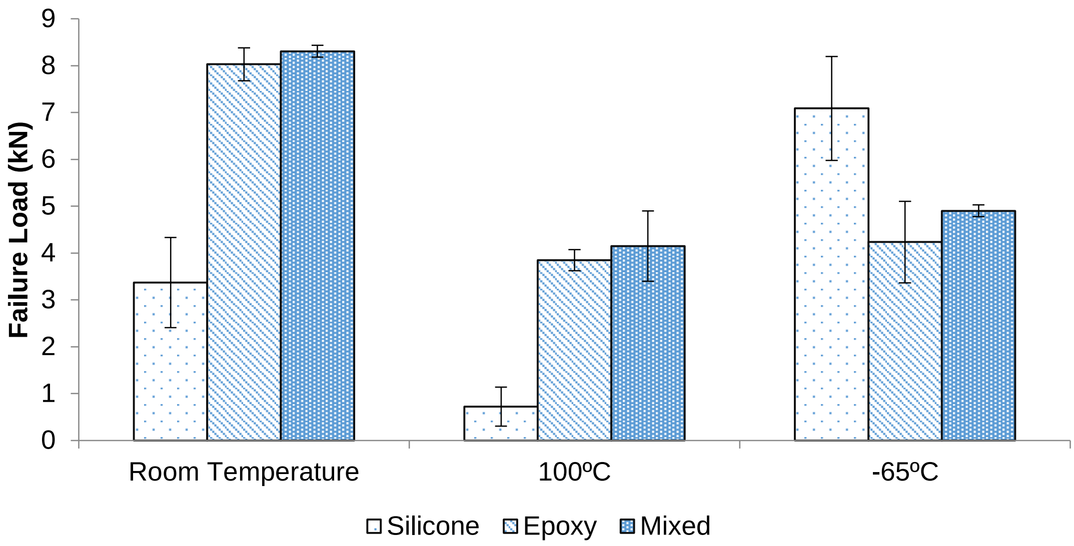

Figure 14 - Static testing results [5]

At room temperature there is a large similarity in results between the mixed adhesive joint and the joint containing only epoxy, while the silicone joint provides smaller loads. These results change with temperature, with the silicone joint being very strong at low temperature and the mixed and epoxy joints being the best at high temperatures.

Results obtained from experimental work and numerical simulation were compared. Typical experimental curves were considered. Experimental and numerical P-δ curves allowed the study of stiffness, the maximum load and the displacement of the joints at room temperature. A comparison of these curves can be found in Figure 15.

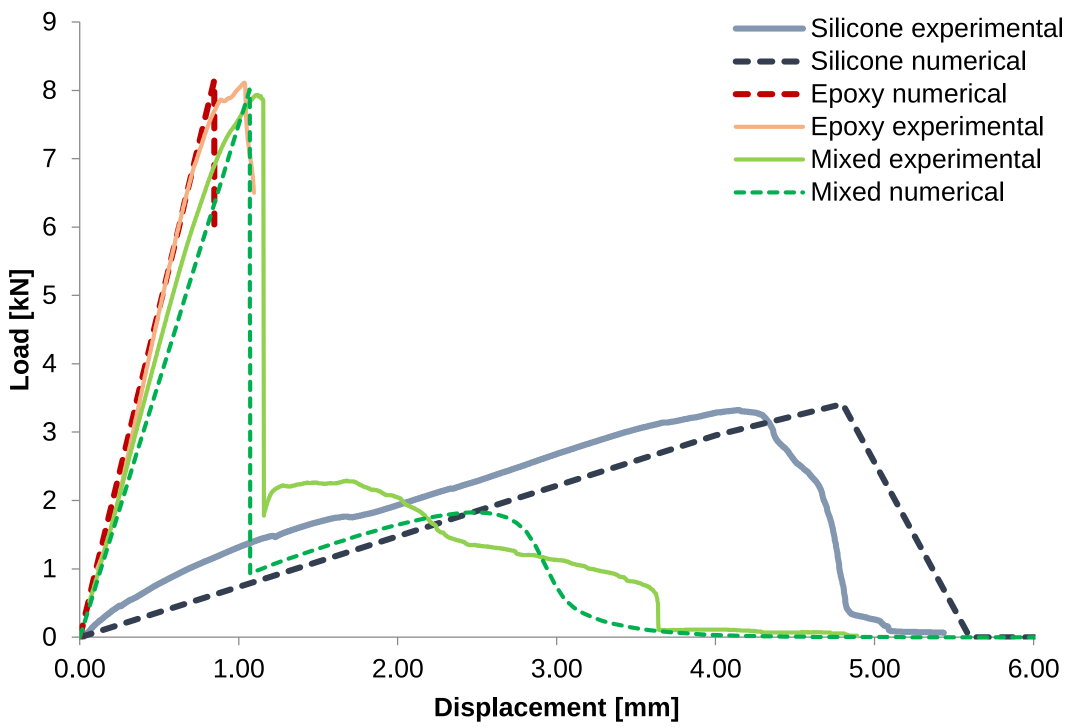

Figure 15 - Experimental and numerical load displacement curves for the tested joints

In both the numerical models and experimental tests the silicone specimens were found to always break cohesively in the silicone layer and the epoxy specimens were found to break in the ceramic layer. The mixed adhesive joint exhibited cohesive fracture in the ceramic near the epoxy layer but, after the test was stopped, the silicone layer was still intact and able to carry a small load, achieving a displacement at failure comparable to the silicone joint and nearly five times larger than that of the epoxy joints. This secondary load increase can be seen in the graph, with a dual behaviour of the mixed adhesive joint, which after reaching its maximum load, it still has a substantial amount of displacement before total failure. Both the finite element model and the experimental tests captured this phenomenon.

A good agreement between experimental and numerical data was generally found. In the initials peaks (after the elastic phase) a small error can be found, as the simulation curves cannot match the slight reduction in stiffness near the maximum load. This is due to the triangular CZM law adopted in ABAQUS®, which does not allow the displacement to increase with constant force. A trapezoidal cohesive zone model would be able to more precisely simulate this part of the graph, albeit with increased complexity. The other main divergence between cohesive model and experimental data can be found in the curves relating to the mixed adhesive joint, immediately after the first peak. The first peak corresponds to the failure of the ceramic tile, while the second peak is due to the load being transferred to the still intact silicone layers. This second peak is very hard to model, because in the experimental specimens there is significant drag caused by the interference of the broken (and now sliding) materials against the adhesive connections still remaining in place. The modeled curve can therefore roughly match the forces and displacements but is not able to accurately simulate the unstable nature of the load progression.

5 Conclusions

In this work, a numerical simulation was developed to simulate ceramic-metal joints at room temperature. Joints with a high strength/high temperature epoxy (XN1244) and a RTV silicone (RTV106) were manufactured and tested in a specially designed apparatus in order to validate the numerical simulation. In an attempt to explore the synergetic advantages of a combination between these two materials, mixed adhesive joints were produced.

In the experimental procedure presented in this work, RTV106 silicone joints were found to exhibit low strength when compared with the other configurations studied. In fact, the maximum load measured for the silicone was 3500 N, while the other joints reached around 8000 N. On the other hand, the maximum displacement measured for the silicone joints was about 5 times larger than the displacement of the epoxy joint. In the mixed joint, the maximum load reached was the same as in the epoxy adhesive joints, but with a slightly higher deformation obtained.

All joints failed cohesively during these tests. The joints using only RTV106 silicone had cohesive failure in the adhesive, while the joints that used XN1244 had cohesive failure in the ceramic substrate. In the mixed joint, even after the ceramic near the epoxy breaks, this type of joint can still absorb some amount of load, as the silicone layer and the ceramic next to it is still reasonably intact. The brittle nature of the XN 1244 epoxy joints was partially corrected with the addition of RTV106 to the joints resulting in a stronger and safer joint.

For the numerical simulations, the first step consisted in the determination of the mechanical properties of the ceramic and adhesives for implementation in the cohesive models. The ceramic parameters were successfully determined by means of an inverse method while the adhesive properties were gathered and completed.

The second step necessary to develop the finite element models was the determination of representative boundary conditions. The boundary conditions were mainly represented by spring elements whose stiffness was determined by comparing the movement of the actual joint during experimental work with the movement of the simulated joints.

With the properties and the boundary conditions correctly defined, a full cohesive model was implemented for each type of joint used. The P-δ curves obtained with this finite element analysis models were found to be in good agreement with the experimental results, thus validating the simulation procedures. This model will be used for an optimization procedure, focusing on geometrical changes intended to maximize the mechanical strength of this type of joint.

Acknowledgments

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Nagase-Chemtex is also gratefully acknowledged for free supply of adhesive.

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Paper 6

Geometrical study of mixed adhesive joints

Geometrical study of mixed adhesive joints for high temperature applications

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Abstract

The use of adhesives for high performance, structural applications has significantly increased in the last decades, allowing the aerospace and automotive industries to construct lighter and more efficient multi-material structures. However, the use of adhesive joints in adverse environmental conditions is still limited, due to the reduced capability of adhesives to withstand large thermal gradients. Dual adhesive joints, which contain two adhesives with remarkably different mechanical behaviour, are a technique suitable for being used in extreme temperatures. The object of this study is a ceramic-metal joint, representative of the thermal protection systems of some aerospace vehicles. In this paper, several joint mixed joint geometries are presented, studied with recourse to finite element analysis. In a first phase, the three dimensional finite element models and the material properties are validated against experimental data. In a second phase, the model geometry is modified, with the aim of understanding the effect of several changes in the joints mechanical behaviour and comparing the merits of each geometry. The models presented good agreement between experimental and numerical data and the alternative geometries allowed the introduction of additional flexibility on the joint but at the cost of lower failure load.

K**eywords:** Dual adhesive joints; High-temperature adhesives; Low-temperature adhesives; Cohesive elements;

1 Introduction

Adhesive joints are a commonly used joining method employed by many technologically advanced industries. Among these industries, the aerospace industry is one of the main users, exploiting the adhesives ability to join dissimilar materials and to redistribute loads more effectively, which leads to lighter structures [1]. There are however several aerospace applications where adhesive joints are at the limit of their capabilities, usually due to taxing environmental conditions [2]. The joining of ceramic to metals in thermal heat shields is one of those applications. The use of adhesives is a practical solution for this application, but large thermal gradients, highly dissimilar material properties and varied mechanical loads combine to create complex and overwhelming loadings on the joint. Raphael first proposed the concept of mixed adhesive joints in 1966 [3] and this concept has evolved into a technique that might enable adhesive joint to operate in extreme conditions. With careful selection of the two adhesives used, there is a possibility to reduce the stress concentrations at the ends of the overlap, which are typical for single lap joints and which can induce premature joint failure. A flexible adhesive should be present at the ends of the overlap, while a stiff adhesive must be applied in the central section of the joint, where it will be less subjected to large deformations under loading.

In 1973, Hart-Smith [4] recognized that the use of mixed adhesive joints could yield improvements in the mechanical strength of joints subjected to large temperature gradients. In 2007, da Silva and Adams [5, 6] made use of this concept and predicted improvements in the mechanical behaviour of a joint under a large temperature gradient. In their approach, the adhesives to be combined were not only dissimilar in the mechanical properties, but also in their temperature handling capabilities. Marques et al. [7, 8] performed a series of experimental studies, bonding ceramic tiles to a metallic substrate using a mixed adhesive joint, combining a room temperature vulcanizing (RTV) silicone with a high temperature epoxy. The joints were tested under shear loads at room temperature, -65ºC and 100ºC. With these static tests, mixed adhesive joints were found to have consistent strength at high and low temperature, while providing a good amount of joint displacement in both cases. Figure 1 shows the evolution of a mixed joint strength in a wide range of temperatures.

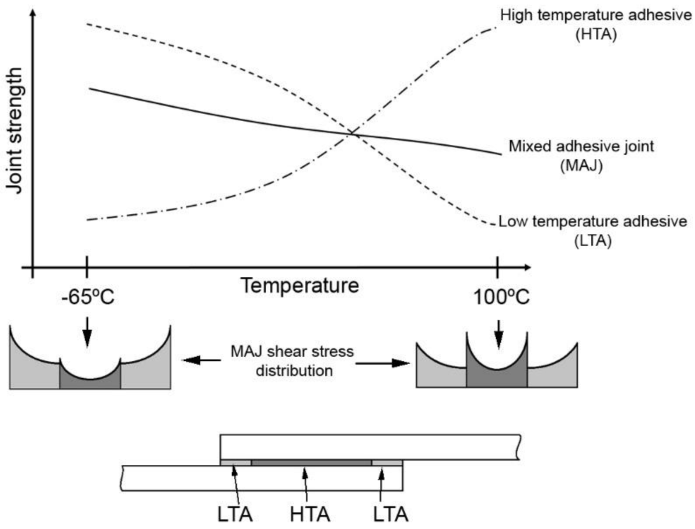

Figure 1- Working principle of the mixed adhesive joint concept.

Various geometrical parameters of an adhesive joint can be changed to improve the mechanical behaviour of an adhesive joint, including mixed adhesive joints. A technique commonly employed to reduce stresses is the use of tapered substrates and adhesive layers. This a very common research subject and various authors [9-18] have employed this technique with good results, always with the aim of lowering the stiffness at the ends of the overlap of a joint and achieve a smoother load transfer.

Another important characteristic that can be controlled in mixed adhesive joints is the ratio of the two adhesives on the overlap, which also causes significant changes in the overall joint strength and behaviour. Srinivas [19] has concluded in his numerical analysis with finite elements (FEA) that optimum lengths of stiff and flexible bonds can be chosen to assure the lowest possible stresses in the bondline. Raphael [1] suggested to select the adhesive ratios so that the stress distributions of both adhesives match. Fitton [20] improved on this by making a numerical analysis, studying the effect of different adhesive modulus combinations and different geometrical configurations. These studies confirmed that that lower shear stresses are obtained when the peak shear stress is equal in both of the adhesives, but he also identified that this concept is not the optimum for achieving strength improvement, instead being more suited for obtaining lower shear stress distributions. Chiminelli et al. [21] numerically modelled mixed joins with aluminium/composite substrates under shear loads. A simple optimization procedure was performed to determine the optimum discrete grading of properties in a bondline and the ultimate load was improved by around a 70%, maximizing the ultimate loading capacity of a single lap joint.

A very powerful tool for studying the behaviour of adhesive joints, including mixed adhesive joints, are cohesive zone models (CZM). These models are increasingly being used to improve the failure load prediction of finite element models and various authors such as Needleman [22], Tvergaard et al. [23] and Camacho et al. [24] were among the first to adapt this technique for use in adhesive joints. A CZM is able to represent the fracture process and location, advancing beyond the typical continuum mechanics modelling. It does this by including in the model a series of discontinuities modelled by cohesive elements, which use both strength and energy parameters to simulate the nucleation and advance of a fracture crack [25, 26]. The relationship between the stresses and displacements is governed by a traction separation law. Figure 2 shows the pure-mode (traction or shear) and mixed-mode traction separation laws, where t_n and t_s are the cohesive strengths in tension and shear, respectively, and δ_n^0 and δ_s^0 are the respective strains, and δ_n^f and δ_s^f are the tensile and shear strains at failure, respectively.

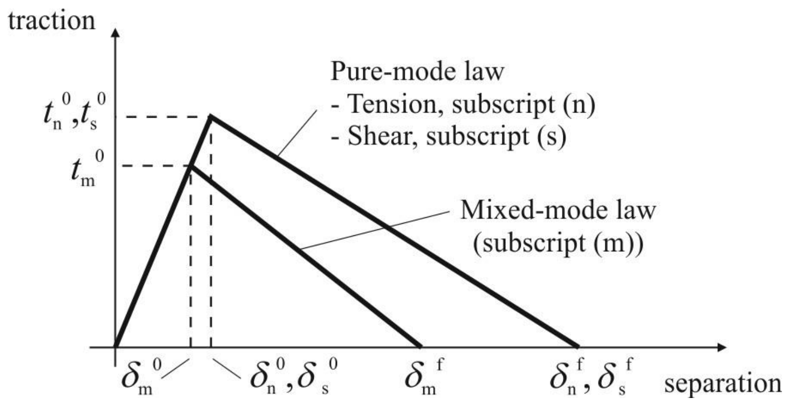

Figure 2 - Traction-separation law with linear softening: pure and mixed-mode models

The shape of this law can be changed to more adequately fit the mechanical behaviour of the simulated material. The initial elastic portion is always kept linear, but in the literature various shapes for the softening portion of the curve can be found. Needleman introduced a shape based on more complex functions such as polynomial [22] and exponential [25] laws. Tvergaard and Hutchinson [23] suggested a trapezoidal model while Liljedhal et al. [28] proposed the simpler bilinear model. Campilho et al. [29] addressed the influence of the CZM shape in the strength prediction of composite single-lap joints, considering different adhesives (brittle and ductile) and overlap lengths. Results showed that the CZM shape is more relevant when considering ductile adhesives, in which case the best results were obtained with the trapezoidal shape law. On the other hand, the results for the brittle adhesive were similar between the three CZM shapes, although the triangular CZM was slightly better. Marques et al. [30] developed a two-dimensional numerical model to simulate ceramic-metal joints using the dual adhesive technique. A flexible silicone adhesive was considered at the bond edges, whilst a rigid epoxy was used in-between. The CZM approach enabled a faithful representation of the experimental load-displacement (P-δ) curves, which validated the simulation procedure.

This work therefore aims to increase the understanding of the mixed adhesive joint capabilities, by mechanically testing metal-ceramic specimens at room temperature and under shear loading and then using this information to allow the construction and validation of a finite element model. To more accurately represent the real joint, the model makes use of cohesive elements, combining a continuum mechanics approach with a fracture mechanics approach. The cracks can therefore be simulated and matched to the cracks identified on the mechanical testing and this process leads to a validated model that can be used for joint optimization purposes.

2 Experimental procedure

2.1 Materials

Success on the use of dual adhesive joints is in large part dependent on the correct selection of adhesives. The adhesives employed in a dual adhesive joint must be not only compatible but only sufficiently different in properties to complement each other. For this work the adhesives selected were a single part epoxy and a RTV silicone. The selected epoxy is a commercially available stiff and brittle adhesive, suitable for high temperature use produced by Nagase-Chemtex (Osaka, Japan) under the reference XN1244. This adhesive is a one component, high temperature, paste epoxy adhesive, with a glass transition temperature (T_g) of 170ºC. Due to its T_g it provides good mechanical properties up to 150ºC [31]. The cure process is heat activated and requires exposure to a temperature of 140ºC during 1h to achieve complete cure. The RTV silicone is also of a commercially available type, produced by ACC Silicones LDT (Bridgewater, UK) under the reference RTV106. This adhesive is very distinct from the XN1244 epoxy by being a very ductile and flexible material, with much lower mechanical strength. RTV106 has a much lower T_g (around -130ºC), which makes it more insensitive to low temperatures, maintaining a good level of strength while the epoxy becomes extremely brittle.

The curing process of the RTV106 adhesive is very distinct from the curing process of the XN1244 epoxy, by being based on the absorption of humidity from the air [32]. In order to ensure a complete cure, water molecules must diffuse from the surface of the material to the interior. Due to the reduced mobility of water molecules, this cure is a slower process. When thick layers of adhesive are used, curing times as long as 10 days can be required to obtain full cure. The properties of these two adhesives are listed in Table 1.

Table 1- Mechanical properties of RTV 106 silicone and XN1244 epoxy at room temperature [33-37]

Property	RTV106 silicone	XN1244 epoxy
E - Young's Modulus (N/mm^2)	1.6	5870
G - Shear Modulus (N/mm^2)	0.86	2150
t_n^0 - Tensile Strength (N/mm^2)	2.3	68.23
t_s^0 - Shear Strength (N/mm^2)	1.97	37
G_n^c - Mode I fracture energy (N/mm)	2.73	0.47
G_s^c - Mode II fracture energy (N/mm)	5	2.2

These properties can also be visualized as the traction separation laws, used to govern cohesive finite element simulations. Figure 3 shows the shape of those laws for both adhesives. Figure 3a) represents the Mode I (traction) law and 3b) represents the Mode II (shear) law.

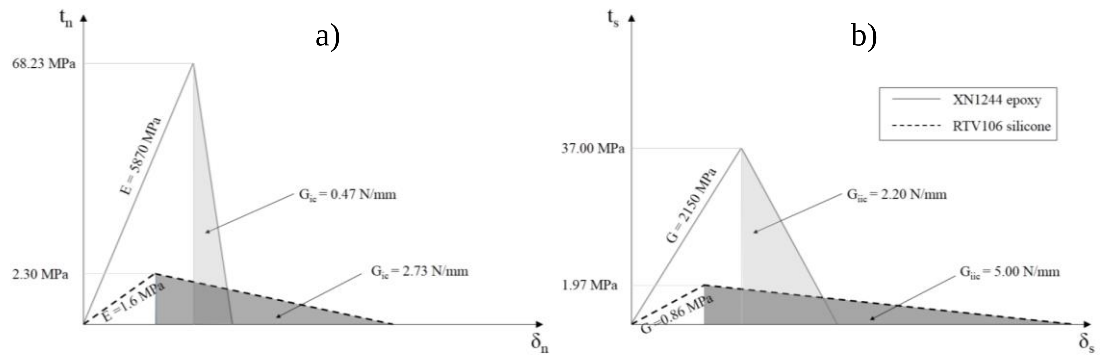

Figure 3- Mode I (a) and mode II (b) triangular traction separation laws for the adhesives.

The metallic substrate of the dual adhesive joint is machined from an aluminium alloy of the 6063 T6 type. The ceramic tile used in this work is made of cordierite, a high temperature resistant ceramic. By being able to withstand large temperature gradients, it is a material suitable for the role of thermal shielding. The full mechanical properties of the cordierite material were previously obtained using a reverse characterization method described in a previous paper [30]. Table 2 lists those properties.

Table 2 - Mechanical properties of cordierite at room temperature

Property	Cordierite
E - Young's Modulus (N/mm^2)	5200
G - Shear Modulus (N/mm^2)	2060
t_n^0 - Tensile Strength (N/mm^2)	45
t_s^0 - Shear Strength (N/mm^2)	45
G_n^c - Mode I fracture energy (N/mm)	0.5
G_s^c - Mode II fracture energy (N/mm)	0.5

2.2 Experimental specimen configurations and geometry

The specimens studied in this work consists of a ceramic tile bonded to a metallic sheet, as shown in Figure 4. Three specimen configurations were tested in the experimental phase. All three configurations use the same substrates but differ in the adhesive layer used. One configuration used an adhesive layer with RTV silicone adhesive, other used XN1244 epoxy and finally the third combination uses both simultaneously in a mixed adhesive joint.

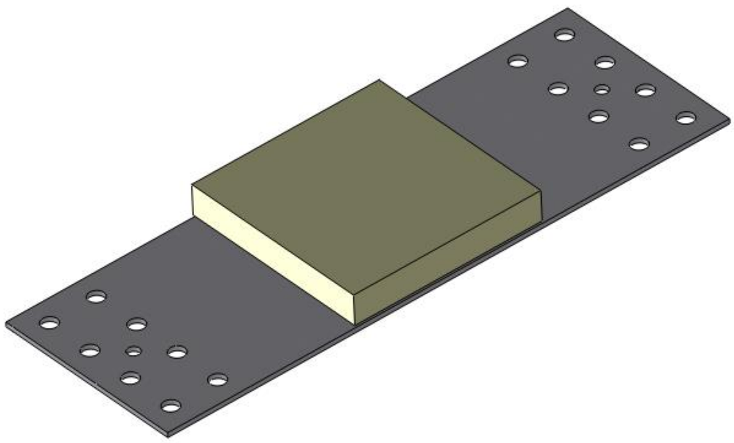

Figure 4 – Three-dimensional drawing of the specimen used.

The ceramic tiles had a dimension 80x80x12.8 mm^3 and were produced by water-jet cutting of a larger plate. They were bonded to the centre of the aluminium sheet using three different configurations of adhesive layers. The area available for bonding is 60x60 mm^2, slightly smaller than the area of the ceramic substrate (80x80 mm^2). A detailed drawing of each configuration and its geometry is shown in Figure 5.

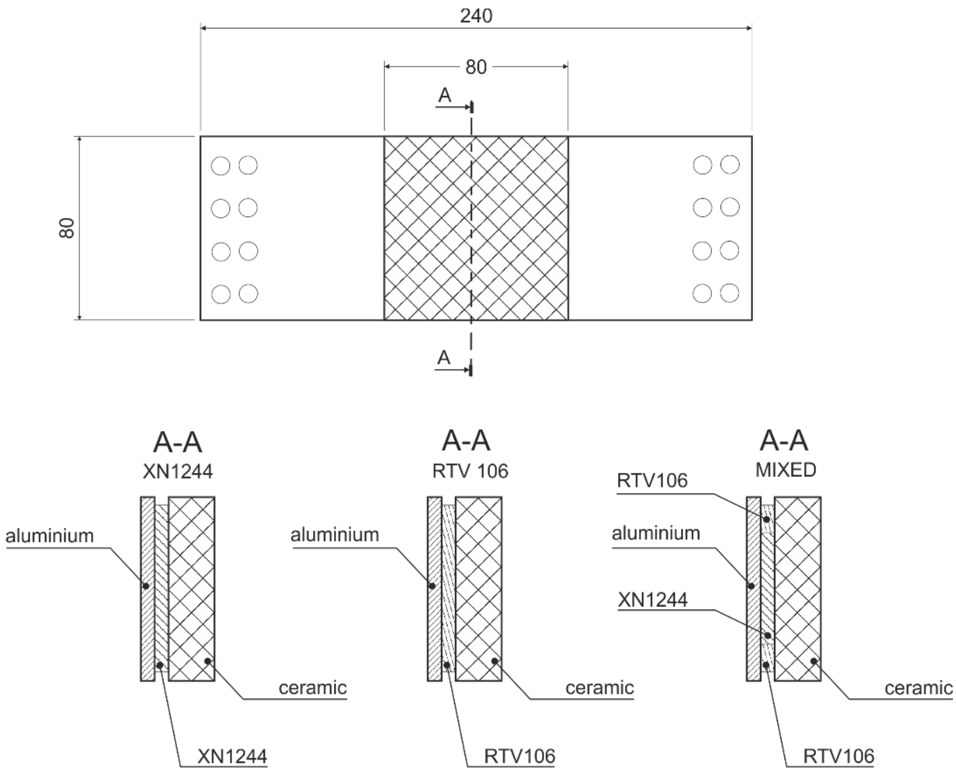

Figure 5 - Schematic view of the experimentally tested configurations

An important parameter to define in a study of mixed adhesive joints is the ratio between the two adhesives. This ratio can be defined using a variety of parameters, but in this work the adhesives surface area was used to calculate a simple ratio, dividing the area of the silicone layer ($A_{silicone}$) by the area of the epoxy layer (A_{epoxy}). The mixed joint tested here has a ratio of 0.5. Table 3 lists the bonded area and ratio (if applicable) of each of the specimens tested.

Table 3- Bonded area configurations for experimentally tested specimens

Bonded area configuration	**$A_{silicone}/A_{epoxy}$ ratio**
60x60 mm^2 Epoxy	Full Epoxy
40x60 mm^2 Epoxy, 20x60 mm^2 Silicone	0.5 - Mixed joint
60x60 mm^2 Epoxy	Full Silicone

A thick adhesive layer (1mm) was used to ensure strength of the RTV silicone adhesive. While theoretically a thinner adhesive layer would provide higher joint strength improvements in comparison to a single brittle adhesive (because the load would be more concentrated at the ends of the overlap), in practice the use of the RTV silicone in thin layers results in very weak joint strength due to its extremely low modulus of elasticity. A frame of silicone rubber, 1 mm thick, was cut to constrain the adhesive underneath the ceramic tile and to set the adhesive layer thickness. Two different techniques were used to manufacture the single adhesive joints and the mixed adhesive joints. The latter type, instead of having a full, unobstructed internal square of 60x60 mm^2, has two thin barriers dividing the square into three different bonding areas. This avoids the contact between the two different adhesives. A custom mould (shown in Figure 6) was built to position and restrict the movement of the substrates during the curing process.

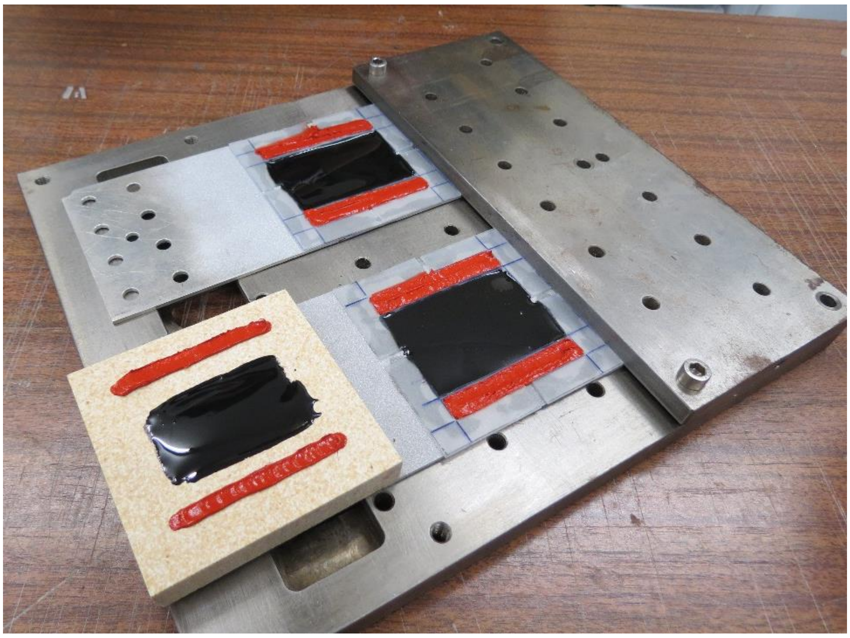

Figure 6 - Specimens in the mould, ready for bonding.

2.3 Static testing procedure

The specimens were tested in a universal testing machine using a custom testing tool, designed to fix the metal substrate while the ceramic tile is pulled away. This introduces a shearing load in the adhesive layer. The testing machine is an INSTRON (Norwood, MA, USA) model 3360 electromechanical testing machine with a load cell of 30 kN. The selected test speed was 1 mm/min and the temperature was 22ºC (room temperature). The load-displacement curve (P-δ curve) was registered during the test allowing a variety of properties regarding the whole specimen to be determined: stiffness by the slope of the curve in the elastic zone, the maximum load P_{max}, and the maximum displacement δ_{max} at failure.

2.4 Testing tool compliance measurement

The testing tool used for this work is not standardized and its substantial size and asymmetrical shape was found to introduce additional deformation when the specimens were tested. To quantify the additional deformation a simple test was performed, using a steel dummy specimen with high stiffness. The measured displacement in this calibration test can be then removed from the displacement measured during the experimental test to obtain a P-δ curve without contribution from the testing tool displacement.

The dummy specimen, show in Figure 7, was constructed with welded steel plates. A simple FEA was carried out to ensure that the stiffness of the specimen was maximum and negligible when compared with the experimental testing results.

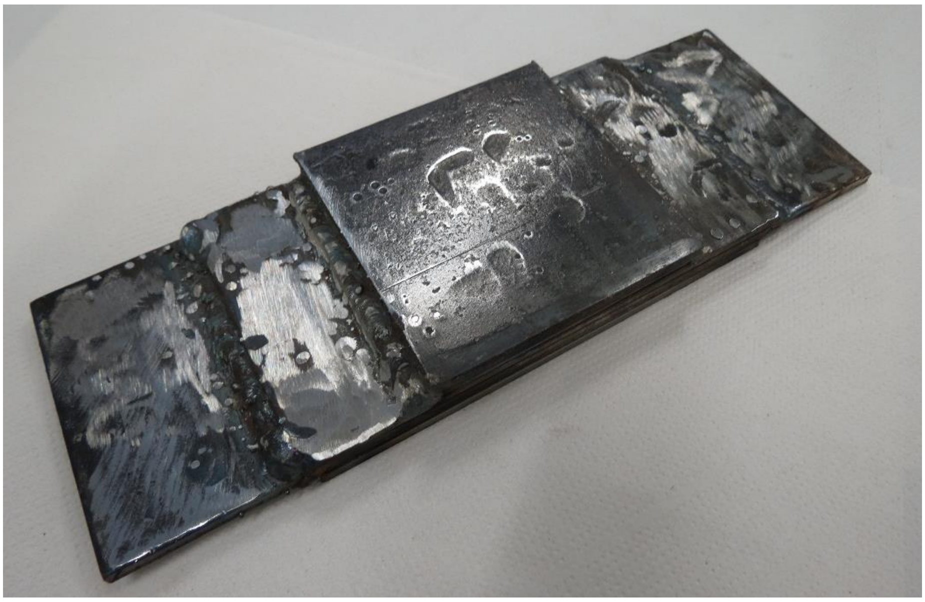

Figure 7 - Dummy specimen used for compliance measurement

The dummy specimen was fastened to the testing tool in a manner equivalent of the other experimental specimens. It was then gradually loaded to a maximum load of 10 kN and the resultant *P-δ* curve registered. This curve is therefore a representation of the testing tool displacement for each given load value. This compliance curve was curve-fitted and used to find a displacement per load equation (Figure 8).

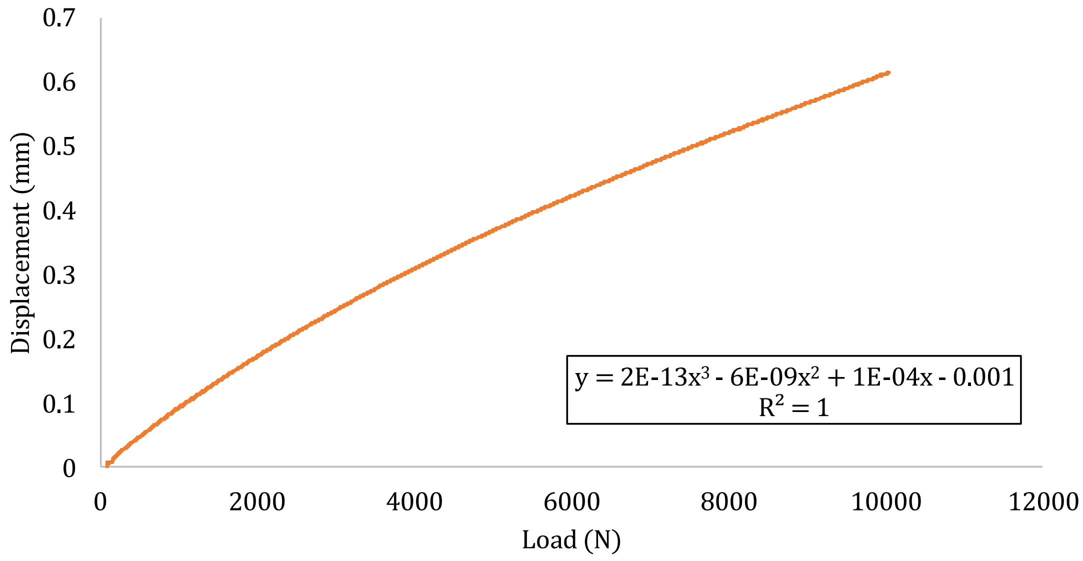

Figure 8 - Compliance curve of the testing tool and respective compliance equation

The compliance equation was then used to subtract the excess displacement from the experimental *P-δ* curve. This process is depicted in Figure 9.

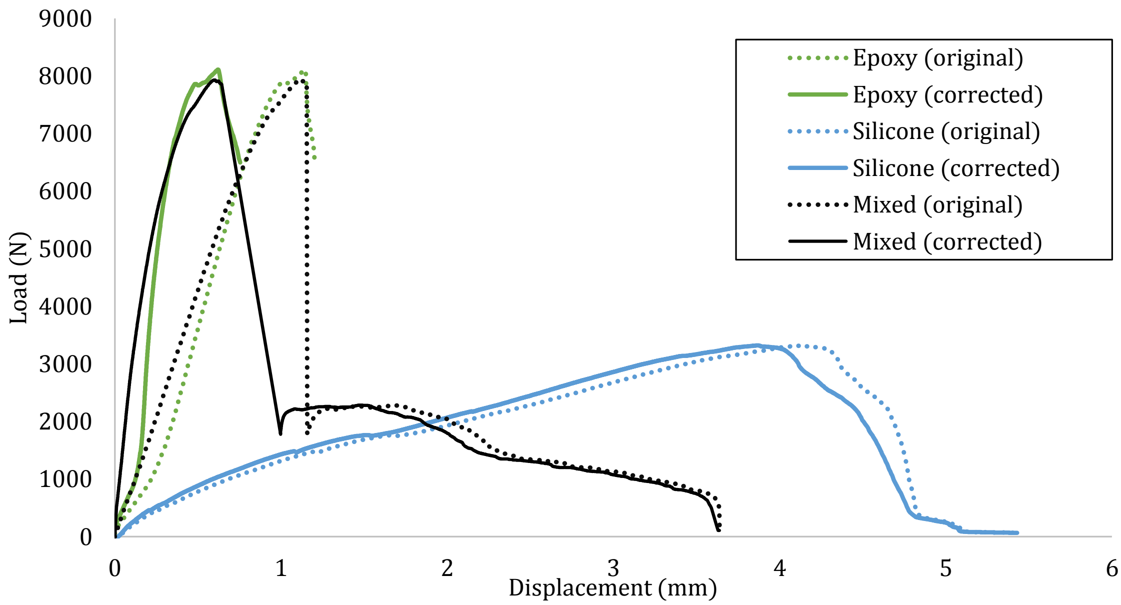

Figure 9 – Correction process of experimental P-δ curve using the compliance equation.

3 Numerical procedure

Finite element analysis was employed to model the specimens' behaviour. The finite element models were validated against the experimental data and were then used to run an optimization procedure. To study the adhesive joint the finite element program Dassault Systèmes ABAQUS® (Vélizy-Villacoublay, France) was used. Cohesive elements model the crack propagation in the specimens, providing a simulated *P*-δ curve and failure load predictions. The cohesive element used for this purpose was of the COH3D4 type, available in ABAQUS® default element library for 3D models. This element allows the use of a triangular traction separation law with linear softening. Due to the extremely computation intensive nature of the 3D cohesive models, some simplification steps were undertaken. Using symmetry considerations, only half of the joint was modelled and the mesh was finely adjusted to reduce the number of elements in non-critical parts of the model. The boundary conditions were similar for all models created and are shown in Figure 10.

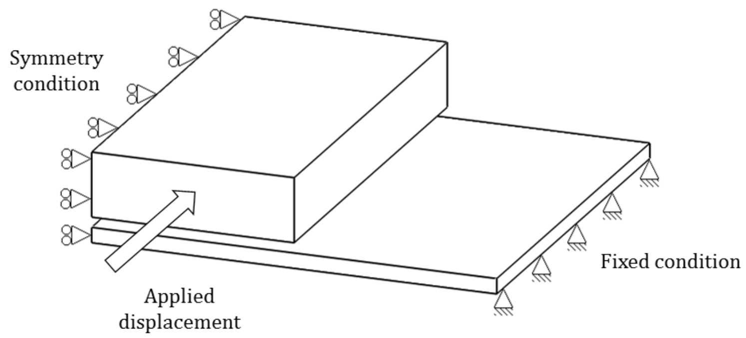

Figure 10 – Boundary conditions used in all finite element models.

3.1 Finite element model validation procedure

To perform an initial validation of the finite element analysis (FEA) models, three different 3D models were created in ABAQUS®, representative of each type of joint configuration that was experimentally tested: adhesive layer with silicone (silicone joint), adhesive layer with epoxy (epoxy joint) and adhesive layer with dual adhesives (mixed joint). The models employed cohesive elements, with the aim of achieving a complete modelling of the failure procedure. A cohesive analysis was performed for each of these three configurations. The cohesive models made use of thin layers of cohesive elements, placed in the middle of elastic elements and the behaviour of each model was simulated until failure. The main challenge in the construction of these models is the location of the cohesive element layers, which must be manually placed in the areas where failure is expected. Figure 11 shows a scheme with the location of each layer for the two main types of specimens.

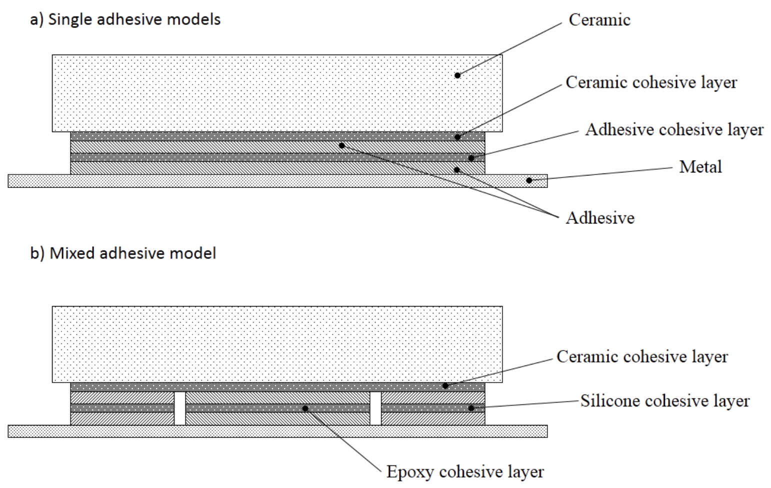

Figure 11 - Location of cohesive layers in finite element models (dimensions exaggerated).

The model of the joint containing silicone adhesive had two different layers of cohesive elements (Figure 11a). A cohesive layer was introduced in the bottom portion of the ceramic tile and the middle of adhesive layer. The thickness of the cohesive layers was 0.1 mm, much thinner than the actual adhesive layer thickness which is 1 mm. This low value was necessary to correctly use the cohesive elements as is also the same thickness present in the models and specimens used to determine the ceramic properties. This ensures consistency in the use of cohesive elements.

The model of the joint containing epoxy adhesive (also Figure 11a) is similar, with a thin layer of cohesive elements placed in the middle of the adhesive and another layer of cohesive elements was located in the ceramic tile, immediately above the bonding line. The configuration of the cohesive model for the mixed adhesive joint (Figure 11b) is the most complex as it has four different cohesive element layers. There is a layer for the lower portion of the ceramic, one in the middle of the epoxy adhesive and two additional layers located in the middle of each silicone section. This geometry allows the cracks to appear and propagate in each of the adhesives and in the ceramic. The model geometry and mesh are shown in Figure 12.

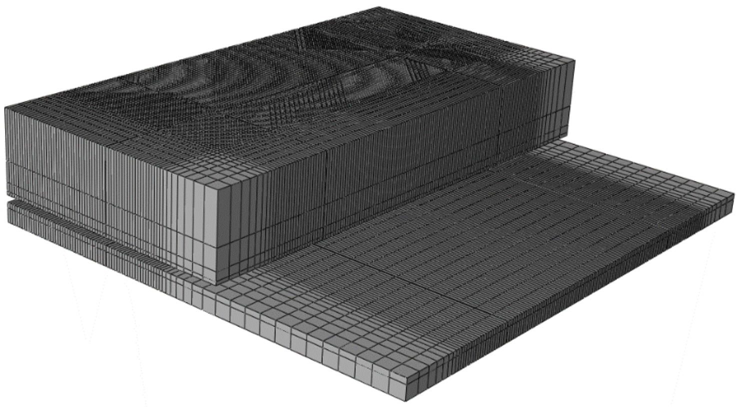

Figure 12- Finite element model of mixed adhesive joint.

3.2 Study of alternative configurations

In an effort to understand the effect of geometrical changes on the studied mixed adhesive joint, several alternative joint configurations were proposed and numerically studied. A description of these configurations are described next.

Square mixed joint

To simplify manufacturing, the orientation of the layers of adhesive in the previously described mixed adhesive joints is such that they are optimized to handle loads only in one direction. While this is sufficient to study the mixed joint concept, in real world applications it might be preferable to develop a joint geometry that is able to handle loads in more than one direction. To achieve this purpose, an alternative mixed adhesive joint geometry was modelled using a silicone adhesive layer that encompasses an internal epoxy square. For clarification, a simple comparison between the experimentally tested mixed joint and this square joint is shown in Figure 13.

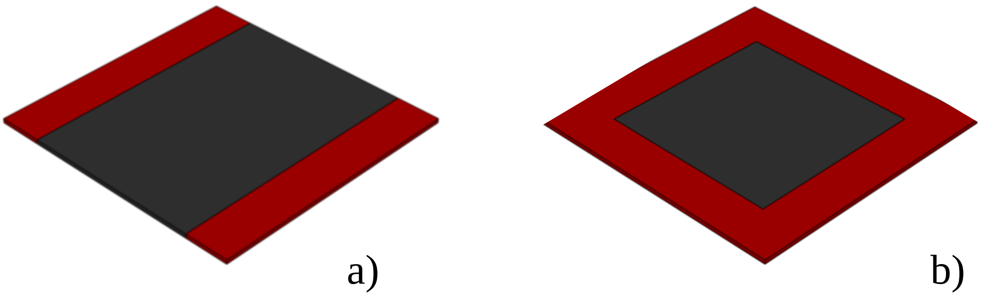

Figure 13- Mixed joint experimentally tested a) and proposed square mixed adhesive joint b).

In this squared layer, the maximum displacement zones created by any type of side loading on the ceramic tile will always occur in a zone of the adhesive layer that is composed of silicone adhesive. By using the same dimensions of the previously described mixed adhesive joint and adding symmetry, this model has more silicone in the adhesive layer. This translates into a $A_{silicone}/A_{epoxy}$ ratio of 1.25, higher than the 0.5 of the initially proposed mixed joint.

Ramped joint

A technique that can modify the behaviour of dual adhesive joints consists of the use of a tapered adhesive layer, gradually increasing the amount of adhesive in the overlap ends. A model employing such technique was modelled using finite elements and its basic geometry as shown in Figure 14.

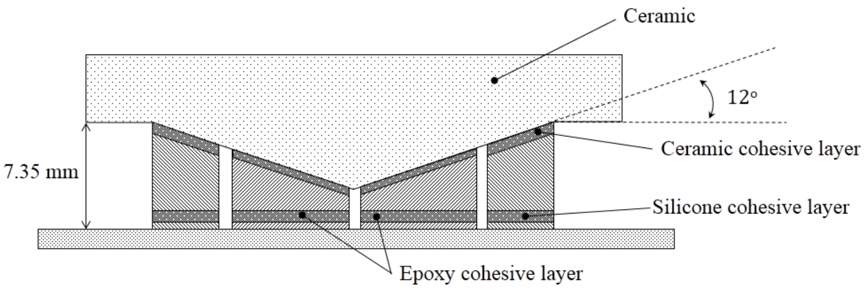

Figure 14- Schematic drawing of the ramp mixed adhesive joint and cohesive layer locations.

This model has an adhesive layer that varies from a 1 mm thickness in the centre of the joint to a 6.35 mm thickness in the joint extremities. This means that the part of the layer containing epoxy adhesive has the same thickness of the flat joint while the thickness in the silicone section is significantly thicker. The value of the angle was selected to be as big as possible without weakening the ceramic tile. This joint was modelled to have a bonded area ratio equivalent to that of the experimentally tested mixed adhesive joint.

The general aspect of the finite element model and its mesh is shown in Figure 15.

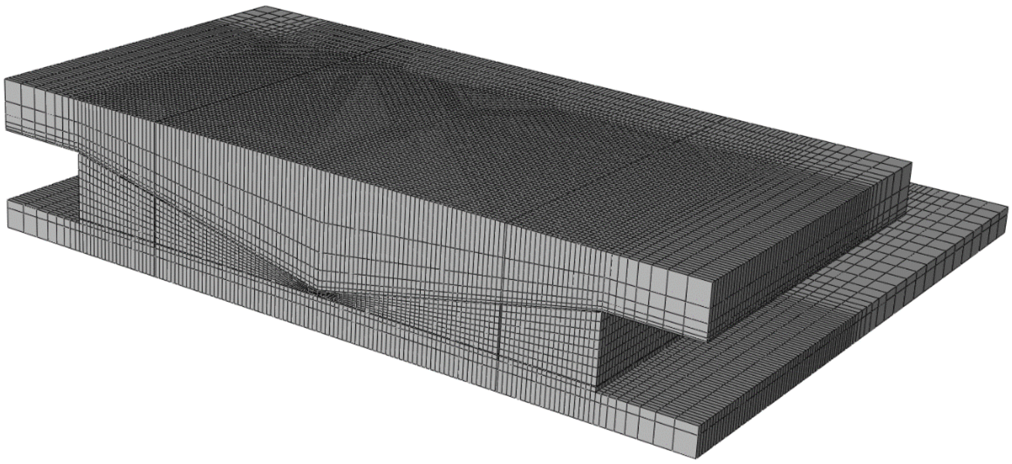

Figure 15- Finite element model of ramp mixed adhesive joint.

Table 4 lists the three mixed joint configurations previously described, defining the surface bonded areas and the $A_{silicone}/A_{epoxy}$ ratio for each one.

Table 4- Bonded area configurations for square mixed joint.

Configuration reference	Square joint bonded area configuration	$A_{silicone}/A_{epoxy}$ ratio
Initial	40x60 mm^2 Epoxy, 20x60 mm^2 Silicone	0.5
Square	40x40 mm^2 Epoxy, 2000 mm^2 Silicone	1.25
Ramp	40x60 mm^2 Epoxy, 20x60 mm^2 Silicone	0.5

Ramped joint (other adhesive ratios)

Besides using the same area ratio (0.5) employed in the analysis previously described, the ramp model was further explored by using five additional configurations to assess the influence of the adhesive distribution on the mechanical behaviour of the specimen. The selected configurations and surface ratios are shown in Table 5.

Table 5- Bonded area configurations for the ramp mixed joint.

Ramp joint bonded area configurations	$\boldsymbol{A_{silicone}/A_{epoxy}}$ **ratio**
60x60 mm^2 Epoxy	Full Epoxy
50x60 mm^2 Epoxy, 10x60 mm^2 Silicone	0.2
40x60 mm^2 Epoxy, 20x60 mm^2 Silicone	0.5
30x60 mm^2 Epoxy, 30x60 mm^2 Silicone	1
20x60 mm^2 Epoxy, 40x60 mm^2 Silicone	2
60x60 mm^2 Epoxy	Full Silicone

These models range from a specimen containing only epoxy to a specimen containing only silicone and include four other configurations in between.

4 Results and discussion

4.1 Numerical-Experimental curves comparison

The models initially developed focused on the validation of the properties, boundary conditions and simulation techniques employed in this work, using a comparison against experimental data. Figure 16 shows the results of this validation study.

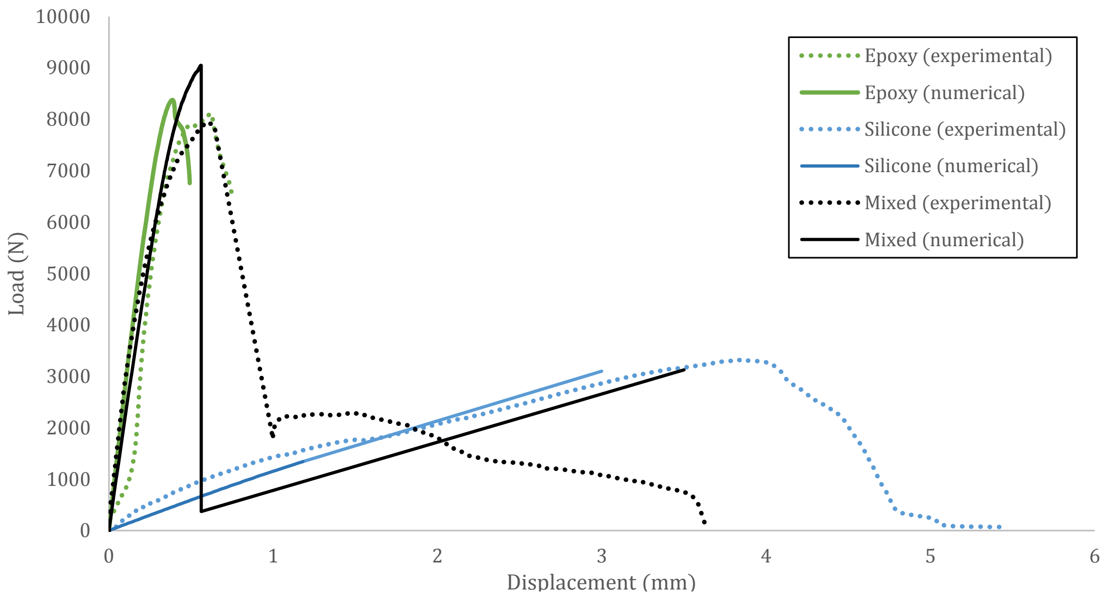

Figure 16 – Experimental and numerical curves of the specimens used for the finite element model validation procedure.

The numerical results obtained with the 3D CZM can be described as having good agreement with experimental data, especially in regards to the maximum failure load. There is also good agreement with the experimental specimen stiffness, demonstrating the importance of the previously described calibration procedure. There was however difficulty in accurately modelling the behaviour of the ductile silicone adhesive. In the silicone only model and the mixed adhesive model it became impossible to model the last portion of the joints mechanical behaviour. The large displacements and relatively small loads involved are not especially suited to the triangular cohesive elements used, suggesting that the use of a trapezoidal or exponential cohesive element law could probably yield improvements. However, the failure mode of the mixed adhesive is relatively complex, which leads to introduction of friction after the initial failure of the epoxy layer and creates further problems in the correct modelling of this phase of the joints behaviour.

4.2 Mixed joint configurations

Figure 17 shows a comparison between three different finite element analysis configurations. Numerical *P-δ* curves are shown for the original mixed joint, the squared joint and a simple ramped joint.

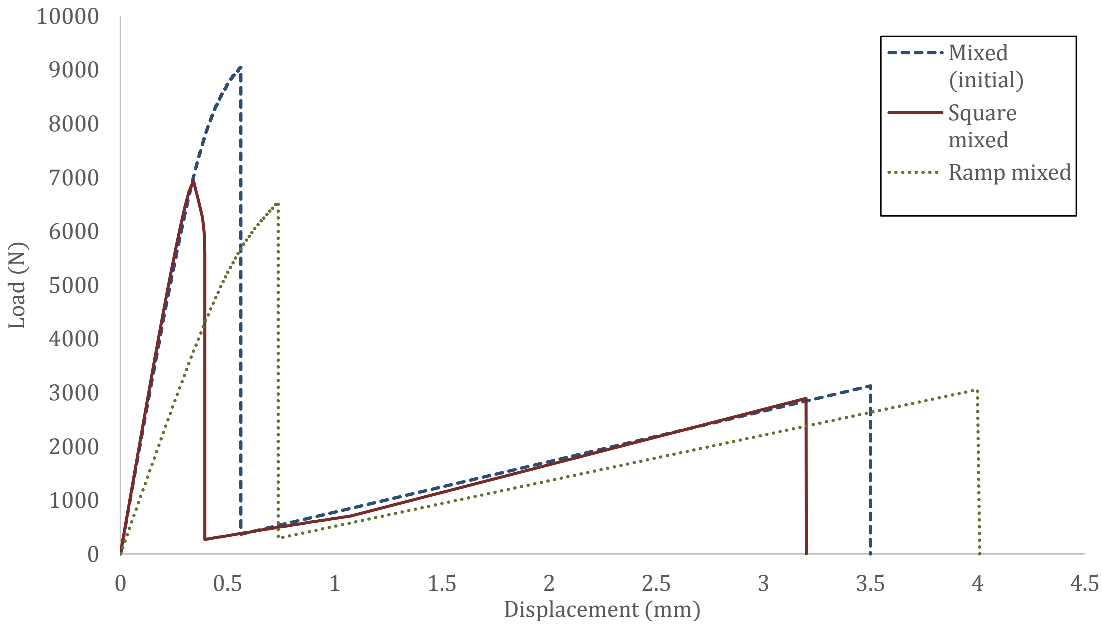

Figure 17- Numerical P-δ curve for the three main mixed joint configurations tested.

This data demonstrates that the initial, simpler mixed configuration is clearly stronger than the other two proposed configurations. The symmetrical squared joint exhibits a large reduction in joint strength, mainly due to the reduced amount of epoxy present in the central section of the overlap, now partially replaced by a border of silicone. However, the overall stiffness of this type of joint is equivalent to that of the initial mixed joint. While the ramped joint exhibits substantially lower failure load when compared to the standard mixed joint, the failure occurs at a larger displacement. In this case, the difference is the ramp geometry and the large amount of flexibility that this configuration introduces on the joint. While this is not directly translated into an increase of peak load, the decreased stiffness is beneficial to a joint that will be subjected to large thermal gradients. All the joints also exhibit a two phase failure, where after an initial maximum load and failure in the epoxy section, the silicone is still able to sustain some load. Figure 18 shows the numerical *P*-δ curves of the ramp models simulated with different adhesive ratios. To allow for comparisons, a numerical *P*-δ curve of the initial (non-ramped) mixed joint is also presented.

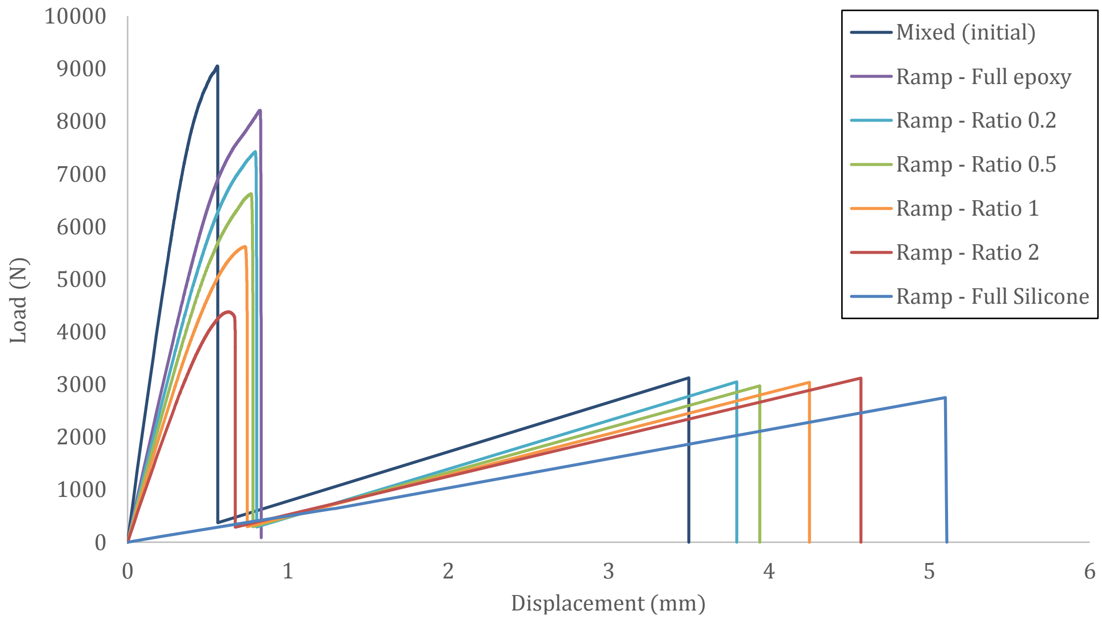

Figure 18- Numerical P-δ curves for the ramped mixed adhesive joints with varying adhesive ratios.

This data shows that using the proposed ramp configuration there is no ratio of adhesive that is able to achieve a strength as high as the flat standard mixed adhesive joint. There are, however, significant changes in the joint initial stiffness. By gradually increasing the amount of silicone in the adhesive layer, the stiffness of the joint is reduced. This reduction in stiffness happens consistently starting from the epoxy-only joint up to the silicone-only joint. Counter intuitively, this reduction of stiffness is also accompanied by a reduction in the displacement at which the maximum failure load occurs. This is caused by the progressively smaller area of epoxy that sustains this initial load peak. Additionally, as the epoxy sections reduce in size the more they are restricted to the thinner central section of the adhesive layer, which also contributes to this early peak load.

5 Conclusions

This work undertook a geometrical study of mixed adhesive joints, using finite element analysis to research the influence of various types of joints. In a first phase, experimental data was calibrated and used to validate 3D finite element models of joints containing different type of layers (mixed and single adhesive). After the successful validation of these models, different geometrical configurations were proposed and their merits studied. The first comparison was between the experimentally tested mixed adhesive joint configuration and two alternative configurations: a symmetrical square configuration, with silicone fully surrounding the epoxy central section and a ramped configuration, with a tapered ceramic substrate and a tapered adhesive layer. The symmetrical and tapered joints were found to have lower failure loads than the standard mixed joint but the tapered joint exhibited significantly lower stiffness, a beneficial characteristic for operation in large thermal gradients. The symmetrical joint presented the same stiffness and lower strength when compared with the standard mixed joint. This was expected and represents the trade-off that must be made to ensure that this type of joint can provide improvements in more than one direction. Lastly, the study of different adhesive ratios on the ramped joint led to the conclusion that an increase in silicone adhesive content translates itself into a consistent reduction in peak loads and joint stiffness.

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